

MICROSTRUCTURE AND PROPERTIES OF LOW-TEMPERATURE PROCESSED
OXIDE AND NITRIDE THIN FILMS

By

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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2002

I would like to dedicate this work to my loving father. He has always served as my biggest supporter in my graduate school career and has always been there for me, contributing his advice, time, and consideration on many different issues. I feel that without his unique perspective on the graduate school process and his unconditional support, my years in graduate school would have been greatly diminished.

ACKNOWLEDGMENTS

I would like to thank a number of people for their support during my graduate school career. First, I would like to thank my advisor, Dr. Rajiv Singh, for his guidance and support. He has continually provided me with the tools that are required to achieve success and this has made for a rewarding graduate school experience. I would also like to thank Dr. Cammy Abernathy, Dr. Arthur Hebard, Dr. David Norton and Dr. Stephen Pearton for kindly participating on my dissertation committee.

Several people played an important part in assisting me with my research. I must thank Dr. Valentin Craciun for his day-to-day guidance with my research. He has provided many hours of discussion and aid, both technical and personal, without which graduate school would have been greatly diminished. He also introduced me to many different areas of research, which will allow me to draw on a lot of different perspectives in my future career. Joshua Howard also has played an important part in my graduate research career, as a discussion partner and laboratory mate and I thank him especially.

I would also like to acknowledge all of the friends and coworkers who made graduate school such an enjoyable time. Mike, Pat, Frank, Jaime, Kyo-Se, Su Ho, Won-Seok, Seung-Mahn, Zhan, Uday, Rob, Brian, Terry, Marc, Frederic, Chad and many others have been good friends and whom I will never forget.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

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December, 2002

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Department: Materials Science and Engineering

This study was designed to evaluate the effect of temperature on the formation of oxide and nitride thin films for a number of different materials systems, including high-k dielectrics, nitrides and transparent conducting oxides.

High K dielectric thin films were pulse laser deposited on silicon and the interfacial layer between the film and substrate was characterized as to the extent of its growth relative to oxygen partial pressure and thickness. X-ray reflectivity and x-ray photoelectron spectroscopy were used to show that there was excess physisorbed oxygen within the film. It was also shown that silicon diffuses through the growing film, especially during the initial stages of film growth, causing the formation of a poor quality interfacial layer.

Passivation treatments of the high-k thin films included the pre-treatments of depositing silicon nitride by photodeposition with UV light. The use of UV light has the effect of lowering the deposition temperature to 300 degrees to grow equivalent film

thickness as that obtained by thermal nitridation at significantly higher temperatures.

Silicon nitride pre-treatments before film deposition had the dual effects of raising the capacitance of the interfacial layer and decreasing the thickness of the interfacial layer. In addition to this, the silicon nitride acts as a diffusion barrier to the movement of silicon into the growing film and metal and oxygen to the lower interface.

Films that were processed with a high-temperature hydrogen anneal displayed a very thin interfacial layer and had the effect of passivating the film from thermal oxide formation. This allowed an increase in capacitance of the film relative to films that had no hydrogen pretreatment.

Indium tin oxide films were processed using mercury-lamp assisted pulsed laser deposition. It was found that the use of UV lowered the deposition temperature and increased the crystallinity of the film and that UV has the advantage of increasing nucleation density during film formation, which leads to the resulting high grain microstructure at the same temperature. High quality films were deposited at a low temperature that had optical properties that were comparable to some of the best values produced in the literature at higher temperatures. It was also found that increased crystallinity led to lower electrical resistivity values in the films.

CHAPTER 1 INTRODUCTION

Background and Motivation

Oxide thin film systems are used in a large variety of applications. These include their use in optical applications, such as optical coatings [Tua00], phosphors such as europium doped yttria [Gao99], transparent conducting films, such as indium tin oxide [Owy00], corrosion resistant coatings, photocatalysts, and as materials for decontamination and purification of environmental pollutants [Pat97]. Some oxides are used as magnetic thin films for memory applications, such as manganates [Pie01], and in ferroelectric applications [Cra99]. Materials such as yttria-stabilized zirconia are being used as template layers for superconducting oxides [Wan01a]. They are also used in transistor structures such as DRAM [Roy98, Ale98, McK98, Gus00] and they are emerging in their potential use as gate dielectrics [Guh00, Sha86, Lee00, Ma99, Kwo00]. These are just a few examples of the diverse uses of oxide thin films.

These materials have been grown using a variety of deposition techniques, ranging from chemical vapor deposition [Tua00, Owy00, Ono99, Kle99] (with all of its varieties) to physical vapor deposition, such as sputtering [Wen00, Cap98, Wil99, Hef97] or laser ablation [Gao99, Pie01, Wan00, Ben98]. With all of these deposition techniques, various processing parameters are key in tailoring the microstructure and composition to display the important properties pertinent to the application of the film. These processing parameters include temperature of deposition, pressure of the deposited species and chemical treatment of the substrate surface.

For many applications, much of the focus for these materials has been on processing parameters for a thin-thick scale (100 nm to >1 micron in thickness) [Gao99, Pie01, Hef97, Ben98, Fra01]. Since the interfacial interaction layer between the film and the substrate has a much smaller scale than the overall thickness of the film, the microstructures of these films were tailored for other properties that are prevalent through the bulk of the film, such as grain size, texture [Hef97], density, stoichiometry [Cra99] and refractive index [Fra01]. Recently, for several applications which require a thickness less than 10 nm, the interaction of the deposited film with the substrate has become one of the most critical areas of study since these films are being reduced to lower thickness. Fueled mostly by aggressive miniaturization of transistors in the microelectronics industry [Fra01], the study of compatibility of the film with the substrate and the initial stages of film growth have proven to be areas of immense importance. With these small length scales, temperature effects, both during film deposition and post-deposition thermal processing, play a dramatic role in the film microstructure and composition.

The desire to scale the device size of both dynamic random-access memory (DRAM) transistors and the gate dielectric in metal-oxide semiconductor field effect transistors (MOSFET) has been the source of much of the research into ultrathin oxide thin films. As the MOS devices continue to decrease in size with each technology mode, the thickness of the dielectric gate has been scaled accordingly, to the point that SiO₂ and oxynitride layers [Buc99], the current materials systems used as gate capacitors, have become so thin (~15Å) that they experience too large direct tunneling leakage currents that make the devices unreliable and difficult to operate. In response to this, films capable of carrying a similar capacitance but having a higher physical thickness in order to reduce the direct

tunneling current have been proposed as replacements. These are called high-k materials, since their dielectric constant is much higher than that of SiO₂ ($\epsilon_{\text{silica}}=3.9$) and include such oxide thin films as ZrO₂, Y₂O₃, Ta₂O₅, TiO₂, and La₂O₃. Following the thickness relationship,

$$t_{\text{high-k}} = \frac{\epsilon_{\text{high-k}}}{\epsilon_{\text{SiO}_2}} \cdot t_{\text{SiO}_2} \quad (1-1)$$

where $t_{\text{high-k}}$ and t_{SiO_2} are the thickness of the high-k film and equivalent oxide thickness of silica respectively and the ϵ values are the dielectric constants of these materials, the high-k films could theoretically be grown to larger thickness (100-50Å) so as to hold the same amount of charge as a thinner, lower-k SiO₂ film and thus prevent direct tunneling.

However, upon their deposition, these films do not hold as much charge as was anticipated. One of the reasons for this is the occurrence of a low-capacitance interfacial layer [Wil01, Buc99, Kan99] that lowers the overall capacitance of the film structure. Other reasons include the microstructure of the film (polycrystalline vs. amorphous vs. epitaxial) [Wil01], stoichiometry [Cra99, Hef97] of the films and stress within the films. Much effort has been invested in exploring the composition and structure of this layer and its response to thermal processing. In addition, it was shown that this layer grew upon annealing steps usually involved in dopant activation after ion implantation that are key to the manufacture of transistor devices.

One of the proposed solutions to the high-k dielectric interfacial stability problem has been a modification of the transistor fabrication order, in which the dielectric may be deposited later in the fabrication order, in order to minimize the amount of thermal processing [Wil01]. It is thus important to explore the possibility of reducing the thermal

budget of film deposition and processing to examine the effects of low-temperature processing on the microstructures of these films.

In order to investigate the effect of low-temperature processing, it is first necessary to examine the mechanism of formation of the interface. There have been many theories suggested about the formation of these interfacial layers, and it is necessary to delineate the various suggested mechanisms of their formation in order to subsequently optimize the film properties for specific applications or eliminate the layer altogether. This research seeks to address issues involved with the formation of this interfacial layer, particularly the effect of temperature on its formation. The characterization of the interfacial layer in more detail will enable us to understand mechanisms of growth and to suggest interfacial engineering schemes to improve the materials properties of the interface.

Several interfacial engineering schemes that have been suggested include the deposition of a nitride diffusion barrier at a low temperature to prevent the formation of the interfacial layer [Cha99, Nie02, Cha01]. Silicon nitride or silicon oxynitride at a monolayer thickness has been proposed because of its well known resistance to dopant diffusion in heavily-doped poly-silicon gates [Wil01, Luc99].

One of the primary techniques that has been suggested for the formation of these monolayers and their thicker oxide counterparts at low temperatures has been the use of UV radiation as a non-thermal energy source [Ish92, Zha02, Ber93]. This technique has the ability order to alter the film stoichiometry, namely of the gaseous reactants within the film[Cra98], and change the crystallinity of the films [Kum02, Cra99]. Successful use of UV-assisted processing may lead to an overall lowering of deposition temperatures,

which may suppress diffusion related problems in the processing of high-k films and allow the use, for other materials systems, such as indium tin oxide, of lower deposition temperature to accommodate polymeric-based substrates [Pai99, Mor02] which may allow more diverse applications of these oxide films.

Dissertation Outline

The objective of this study was to investigate the evolution of the microstructure and properties of oxide thin films that are used for a variety of applications and the effect of low-temperature-related processing on the microstructure and properties of these films. The first investigation centers on the formation mechanisms for high-k dielectric thin films, namely Y_2O_3 and ZrO_2 films, and the development of their interface with silicon. The effect of oxygen stoichiometry, film thickness and surface pretreatment of the substrate are explored.

The next investigation focuses on the development of low-temperature interfacial engineering schemes to protect the silicon substrate from forming a detrimental interfacial layer by nitriding the silicon surface. Silicon nitridation under thermal and UV photodeposition were explored as a means of protecting the interface. The effect of nitridation time, pressure and UV wavelength were explored. The effect of this pretreatment on the interfacial layer and the resistance of this nitride to post-deposition anneals are explored in this section.

The last section examines the effect of UV on lowering the processing temperature for thin films, such as indium tin oxide. The effects on microstructure and electronic properties were explored for this system. ITO was chosen for examination because of its low temperature for amorphous to crystalline transition ($\sim 150^\circ\text{C}$) [Mor02] for physical vapor deposition. With a low temperature system like this, the effect of UV radiation is

more dramatic and can be easily quantified rather than for a dielectric system that is usually deposited at a temperature from 450-650 °C.

Chapter 2 first gives a general review of the subjects of the materials systems that are examined in this study, including the high-k dielectric transition metal oxides, photodeposited and thermally nitrided silicon and indium tin oxide, which falls into the broader category of transparent conducting oxides. This review is followed by a description of pulsed laser deposition, the technique primarily used in this study for thin film deposition, and a brief description of the mechanisms of UV-irradiation of materials for low-temperature applications.

Chapter 3 recounts the experimental procedure used in this study and describes the processing equipment, experimental tabulation and characterization techniques in detail. Chapter 4 presents the results and discussion of the experiments, followed by the conclusions of this study in Chapter 5.

CHAPTER 2 LITERATURE REVIEW

High K Dielectrics

As was discussed in the previous chapter, many deposited oxides have an amorphous interfacial layer between the film and the substrate, regardless of the intended microstructure (epitaxial, amorphous, polycrystalline). This may be due to a lack of thermodynamic stability of the sample, or some kinetic factors, since thin film deposition is a non-equilibrium process.

In order to understand the formation mechanism of this interfacial layer, it is first very important to identify common features about this layer from material system to material system, such as its crystalline structure, composition, and thickness.

Transmission electron microscopy has revealed for many different oxide systems that this layer, upon deposition, is usually 10-20 Å thick [Dim01, Wil01, Yoo01]. Figure 2.1 is an example of a zirconia film deposited directly on silicon from Ramanathan et al. [Ram02] showing an interfacial layer of about 14 Å. It has an amorphous structure, which led many research groups to indicate that it was the HF-last silicon oxide that is thermodynamically stable on Si surfaces, which also has an amorphous structure. However, this structure was not in the stoichiometric relationship SiO_2 , which termed the layer as a sub-stoichiometric oxide [Cha95, Gup01].

In addition to this, many research groups observed that this layer grew in thickness for many systems upon annealing in all kinds of ambient atmospheres [Wil00]. It grew

significantly in O_2 ambients, and in smaller, but still significant amounts in other atmospheres such as N_2 or Ar [Ono99, Wil00].

How and when does this interfacial layer form? The answer to this question must start with the thermodynamics of phase formation.

Oxide Stability in the M-Si-O system

In order to determine the possibility of thermodynamic stability of oxides on silicon, one must first examine the Gibbs free energy of reaction of the ternary thermodynamic system of choice. The reaction



may lead to stable metal oxide formation if

$$\Delta G_{rxn} < 0 \text{ where } \Delta G_{rxn} = \Delta G_{products} - \Delta G_{reactants} \quad (2-2)$$

and if the phase reaction



has a positive ΔG_{rxn} at the temperature of interest.

Hubbard and Schlom [Hub96] performed an extensive investigation of the stability of binary oxides in contact with bare silicon using tabulated thermodynamic data for bulk compounds on silicon at 1000 °C, a designated processing temperature for transistor manufacture and systematically compiled ΔG_{rxn} data for binary oxides on silicon for all of the periodic table. They removed Ta_2O_5 and TiO_2 , two oft-studied oxides for gate dielectrics, from consideration as a stable oxide on silicon as their free energies of reaction tended to favor SiO_2 formation on silicon as opposed to the oxide compounds. However, both Y_2O_3 and ZrO_2 were considered thermodynamically stable on Si, leading

to the idea that these materials could be directly deposited on Si without interfacial reaction.

This approach, however, is complicated by the nature of thin films. Such effects of curvature and entropy minimization associated with mixed solutions (SiO_2 and metal oxide) change the requirements for local equilibrium between thin films and bulk materials. Secondly, the presence during deposition of small partial pressures of gases such as O_2 used for maintaining stoichiometry of the films (an important parameter for optical properties or leakage current characteristics) or ionized species during the deposition make this thermodynamic analysis much too simplistic. Nevertheless, this analysis should be able to predict that an unstable film such as Ta_2O_5 tends to break down upon heating as it moves towards thermodynamic equilibrium while a ZrO_2 film should remain intact to 1000 °C.

Wilk and Wallace offered a thermodynamic basis for the deposition of a $\text{ZrO}_2\text{-SiO}_2$ (called a Zr-silicate) bonded phase on Si with no interfacial layer [Wil00]. Since both SiO_2 and ZrO_2 are stable on silicon according to Hubbard, a mixed $\text{ZrO}_2\text{-SiO}_2$ could be manufactured that maintained stability to 1000 °C.

While the information provided above provides a picture as to the “possibilities” for such phases as yttrium and zirconium silicates and stable interaction of the substrate with the oxides, they are only the starting points for an analysis of interfacial stability. While thermodynamic information is important in determining what reactions are possible, free energies are evaluated under equilibrium conditions. Thin film deposition provides the nucleation and initial growth of the interfacial layer and this most definitely occurs under

non-equilibrium conditions. With that in mind, let us consider previous work that has been performed on thin oxides deposited on silicon.

Interfacial Reactions in the M-Si-O System During Deposition

Evaluation and comparison of different thin films is rather difficult as there are many thin film deposition techniques for oxide films. Each of these deposition techniques has different non-equilibrium conditions. For those films deposited by sputtering and pulsed laser ablation [Cra00a, Wan00], two main theories have been offered for the formation of the interfacial layer. The first is the reaction of the bare Si surface with O_2 present during the deposition. Usually, in order to maintain stoichiometry in the deposited film and to optimize crystallinity (denoted as smallest FWHM in a θ - 2θ x-ray diffraction scan), sputtered and ablated films are deposited under oxygen ambients, usually around 1-100 mTorr. This implies that O_2 molecules are buried within the film during deposition and those close to the silicon surface have an opportunity to react with the substrate.

The second possible source for the interfacial layer is the reaction of ionized species in the plasma with the substrate that leads to sub-stoichiometric bonding with the silicon [Dim01]. It is known that in pulsed laser deposition (PLD), several percent of the total ablated material in the plume is composed of ionized species [Che94]. While this theory is specific to PLD, it is important to analyze when studying my systems in order to understand initial interfacial layer formation and its effect on subsequent annealing experiments. It has also been shown that oxidation is enhanced in the presence of metallic ions [Kim97].

By controlling the partial pressure of oxygen in conjunction with the temperature of the system, an estimate can be made as to the effect of buried oxygen on the interfacial

layer. By controlling the laser energy used to ablate the substrate, one can change the fraction of ionized species striking the Si surface and get an idea of its contribution to interfacial layer formation.

Interfacial Reactions in the M-Si-O System Post-annealing

Several groups were able to grow epitaxial films of Y_2O_3 , due to its good lattice match with silicon ($a_{\text{yttria}} = 10.6\text{\AA} \sim 2a_{\text{silicon}}$) [Cho99, Hun00]. Nonetheless, nearly all of these films have nucleated interfacial layers when they are heated. In other systems that already have interfacial layers upon deposition, it has been observed that these layers grow in thickness upon annealing. Three theories have emerged as to the source of the interfacial layer post-anneal.

The first theory as to the formation mechanism of the interfacial layer is the diffusion of oxygen into as-deposited films from the annealing ambient. Considerable proof has been offered through many oxide annealing experiments in O_2 and other ambients. In some cases where the annealing ambient did not contain oxygen, some authors attribute the formation mechanism to impurities in the annealing ambient diffusing through the film to the Si/oxide interface.

Hunter et al. grew epitaxial Y_2O_3 films on Si(111) using the pulsed laser deposition technique at a base pressure of 5×10^{-9} Torr [Hun00]. They reported no interfacial layer in the as-deposited samples. After annealing to simulate processing conditions in Ar and O_2 , it was observed that an interfacial Si-O layer formed. The authors attributed its formation in the oxygen ambient to diffusion from the surface to the Si/oxide interface. They also attributed the formation in the argon atmosphere to diffusion of O_2 from O_2 contaminated Ar. In addition, they reported the formation of a second amorphous (with a

darker mass thickness contrast in the TEM) layer which they called sub-stoichiometric (oxygen-deficient) Y_2O_3 .

Kang reported ion cluster beam deposited Y_2O_3 films [Kan99] deposited on an oxidized ($t_{\text{silica}} \sim 15 \text{ \AA}$) substrate. Following anneals in Ar and O_2 , they observed the growth of the interfacial layer. The source for the growth, again, was attributed to O_2 from the oxidizing atmosphere. The growth observed in the Ar anneals was attributed to an interfacial reaction between oxygen from the film and the substrate. However, the author observed stoichiometry in the film and thus again attributed the thickness increase to impurities in the ambient. Again, a secondary amorphous layer was observed, in this case labeled an yttrium silicate. Cho et al. [Cho99] observed similar effects in their epitaxial films with the same explanation for the thickness increase.

Some groups, in an attempt to both optimize the chemical structure of the interfacial layer to reduce leakage currents for MOS applications and in an attempt to remove the deposition contribution to the oxide formation, have deposited oxide thin films on thermally or chemically dipped silicon dioxide [Cop00, Cho01]. Subsequently, they have studied the changes in oxide layer thickness as a function of temperature and ambient atmosphere. These studies have yielded some important results, particularly since an additional interfacial layer was observed, which was called silicate layer in some systems.

This layer has been termed a silicate because it has a darker mass-thickness contrast from high-resolution TEM. Some groups have examined this layer recently with XPS and indicated that it consists of M-Si-O bonds that make it a silicate [Wat01].

The formation mechanisms of this additional layer and the reason for its appearance are important points to study. There has been some confusion as to this layer's nature,

with some groups saying that it is only a transition layer between the oxide and interfacial layer [Cop01] and others that describe its growth to high temperatures [Wat01]. By performing a direct chemical analysis of the layer and trying to influence its growth through annealing parameters such as temperature and ambient atmosphere, the formation mechanism of this additional layer can be evaluated.

The mechanism of diffused oxygen from the ambient is certainly an important one in explaining the growth of the oxide layer. Nevertheless, there is evidence that there are problems with this as the only reason for oxide growth during anneals. Namely, the presence of this layer from deposition in many cases leads to the idea that there is oxygen able to diffuse to the interface and react with the Si. This oxygen, if not present in the post-deposition ambient, must be coming from another source: the film.

With some of these annealing studies, however, stoichiometric oxide films were confirmed with RBS or XPS [Ono99]. Further observations have indicated that the ratio of bonded metal to oxygen and the thickness of the stable deposited films remain constant despite anneals in vacuum, N_2 , or Ar while the interfacial layer continues to grow, albeit at a lower rate. Since this has been observed, the presence of excess O_2 within the film has been suggested. Indeed, this excess as not completely bound oxygen has been observed in the Y_2O_3 system [Cra00b] in laser ablated films. The author postulated that the oxygen might reside in the relatively open lattice of cubic Y_2O_3 . Another possible location of excess oxygen could be in the open, higher free energy surfaces of the Y_2O_3 grain boundaries.

As can be seen, there have been many observations about the contributions of different reaction mechanisms that are involved in making the interfacial layer in these oxides. It is

a formidable challenge to a) delineate which of these are occurring in the Y-Si-O systems and the Zr-O-Si systems, b) measure the reaction kinetics of each of these and c) propose methods of suppressing them. Systematic measurements need to be made to sort out the relative contributions of these mechanisms to interfacial layer formation.

Interfacial Engineering Schemes to Suppress Interfacial Layer Formation

There have been several studies undertaken in order to suppress the formation of the interfacial layer and to obtain a layer that may be resistant to further interfacial layer growth under post-deposition annealing. These include the surface pre-treatment to suppress the growth of an interfacial layer through the deposition of a high-density interfacial buffer layer that may block the diffusion of oxygen to the interface. This buffer layer has been proposed to be reacted on the surface of the silicon

Direct Nitridation of Silicon Surfaces Using Ammonia Gas

After silicon oxide-based devices reached dimensions that were sub-0.25 μm ULSI gate length [Hor97], the use of silicon dioxide gate dielectrics became problematic due to the development, mentioned above, of direct tunneling in the films and increasing boron diffusion from the heavily doped poly-Si gate. At that time, silicon oxynitride films became one of the leading candidates to replace SiO_2 . The presence of nitrogen in an oxide thin film has been known to have a number of advantages. These include: a) the suppression of boron penetration from the poly-Si gate, b) resistance to hot electron-induced degradation, and c) a slightly larger dielectric constant since the dielectric constant of an oxynitride increases linearly with the percentage of nitrogen in the film from $\epsilon(\text{SiO}_2)=3.8$ to $\epsilon(\text{Si}_3\text{N}_4)=7.8$. Other benefits include an enhanced resistance to high-field stress and radiation hardness.

Many studies have shown that the manner in which the nitrogen is incorporated into the grown oxynitride film is very important since the dielectric properties depend on the concentration of nitrogen at the surface and the interface of the film. In this regard, there has been an evolution of the processing of silicon oxynitride, from the early days of attempted direct thermal nitridation by ammonia to the current days of nitridation by NO and N₂O gas. Traditionally, nitrogen incorporation by NO or N₂O gas annealing results in a relatively low concentration of nitrogen in the films, on the order of 10^{15} N/cm².

Nitrogen incorporation increases with increasing temperature; so most oxynitride films are fabricated thermally at high temperatures. For more heavily N-doped films, other techniques for nitriding silicon have been proposed, include chemical vapor deposition (CVD) with different precursors and low-pressure (LP) and/or rapid thermal (RT) variations [Gre94, Gus97], jet vapor deposition (JVD) [Ma97], atomic layer deposition (ALD) [Got96] or nitridation by energetic particles (plasma, N atoms, or ions) [Hel92, Kra97, Sch81]. These may result in lower temperature processing conditions but may require post-deposition annealing to minimize defects.

Thermal nitridation of silicon by ammonia gas was originally explored in the 1970's with an aim at nitriding directly the silicon surface through the use of ammonia with the aim of forming not an oxynitride but a layer of silicon nitride for dielectric purposes [Hor97, Ito78]. The direct nitridation of silicon including not only thermal but also plasma-assisted processing, has never been used in practice for a number of disadvantages. These include high-density fixed charges and interfaces states, degraded mobility and a high density of electron traps.

Typically, the direct nitridation of a silicon surface required several processing hurdles that make their use unfeasible. This includes a high reaction temperature ranging from 1100 °C to 1300 °C for 0.5 to 5 hours. Another problem is that the films grow extremely slowly in a self-limiting manner due to the strong blocking ability of the nitrogen to admit further diffusion. Another problem is that long nitridation times lead to amorphous film crystallization and a rough surface morphology [Ito78].

The most important aspect of silicon nitridation that seeks to create a stoichiometric Si_3N_4 film is the suppression of oxidant contamination. Ito reported an experiment with deliberate oxygen doping that showed the refractive index and film thickness very rapidly approached that of SiO_2 with an introduction of greater than 100 PPM [Ito82]. Obviously, the formation of silicon nitride from direct silicon nitridation was deemed impossible.

The bulk phase diagram of the Si-O-N is shown in figure 2.2 [Gus99]. The diagram consists of 4 phases: Si, SiO_2 (cristobolite, tridymite), Si_3N_4 , and $\text{Si}_2\text{N}_2\text{O}$. It can be seen here that the nitride and oxide phases never coexist in bulk form. They are always separated by the oxynitride ($\text{Si}_2\text{N}_2\text{O}$), which is the only thermodynamically stable and crystalline form of silicon oxynitride.

The fact that nitrogen atoms are incorporated at all into SiO_2 at all is puzzling since, according to the thermodynamic equilibrium, nitrogen should not incorporate into a film grown on silicon in almost any partial pressure of oxygen ($p\text{O}_2 > 10^{-17}$ atm), depending on temperature. Nitrogen in bulk SiO_2 or directly on silicon is not thermodynamically stable. One reason postulated by Dimitrijevic et al. is that the nitrogen atoms may be simply kinetically trapped at the reaction zone near the interface [Dim93]. This model is

predicated on the idea that nitrogen reacts only with Si-Si bonds at or near the interface. Another idea is that nitrogen may lower interfacial strain at the oxynitride interface and thus is locally stable at the Si/SiO₂ interface [Doy95]. Non-equilibrium processing has yielded high nitrogen content films, thus lending credence to the kinetic trapping argument. One argument is clear from most experimental observations. All Si₃N₄ films produced contain some oxygen.

One of the most important properties of nitrogen in nitrided layers is that it forms a barrier against the diffusion of boron. In addition to this, it has been shown to lower the diffusion rates of oxygen, NO and other dopants, significantly slowing the rate of further oxidation or nitridation. This ability makes this kind of layer attractive as an interfacial barrier layer at an ultrathin scale. At 900 °C, the continued oxidation of silicon decreases 4 fold with 1-ML coverage of nitrogen at an oxynitride interface.

One argument for the decreased diffusion and hence decreased oxidation is that the density of nitrides is higher than that of pure silicon oxide. In addition, it has been proposed [Gus99] that the N bonded to silicon may make the lattice itself more rigid. It has been shown that silicon interstitials are prevented from diffusing into oxynitride layers [Tsa96], which leads to an increase in density of oxidation stacking faults in the substrate.

Several groups have studied the photodeposition of silicon nitride at a reduced temperature directly on silicon with the idea of producing a silicon nitride dielectric film. For ammonia gas, several chemical reactions occur when it is illuminated by UV light and were reported by Okabe [Oka78].





These reactions allow NH_2 to be in an excited state below 213 nm. NH_3 can be dissociated by UV light of wavelength of 184.9 nm, the reactive state can be produced [Ish92]. Figure 2.3 shows the emission spectrum of a low-pressure Hg source. Ishikawa et al. report that a silicon nitride film may be photodeposited at a temperature of 800 °C to a thickness of about 3-4 nm and a thickness of over 6 nm if a nozzle is used which allows the reaction to occur directly in front of the substrate. In all cases, however, the growth is self-limited. Sugii et al. reported low-temperature fabrication of silicon nitride films using ArF Excimer laser irradiation with a wavelength of 193 nm. They reported a maximum film thickness of 2.5 nm with self-limited growth at a temperature of 400 °C [Sug88] and strong oxygen contamination.

Bergonzo and Boyd [Ber93] reported the low-pressure photodeposition of silicon nitride using a xenon excimer lamp, which emits at 172-nm radiation to photodeposit silane/ammonia mixtures. Again, they reported that ultrapure precursors were required to protect the nitride film from contamination.

Hydrogen Annealing Prior to Film Deposition

Hydrogen annealing poses an interesting possible pretreatment for the prevention of the formation of an interfacial layer, particularly if the interfacial layer is formed prior to deposition. According to Norton et al, the use of hydrogen gas can relax the vacuum requirements needed for the formation of an oxide-free surface [Nor00]. Norton studied this for the GeO_2 system and the concentration of the hydrogen was such that GeO_2 became unstable prior to deposition. This allowed the deposition of an epitaxial film.

Using a similar argument, the passivation of the silicon surface prior to deposition was explored may be high temperature hydrogen treatment so as to eliminate any oxide that may form on the surface.

Indium Tin Oxide

Transparent conducting oxides (TCO) are deposited as thin films and have the unique properties of transparency in the visible region and decent electrical conductivity, with resistivities (ρ) on the order of 10^{-3} to $10^{-4} \Omega \text{ cm}$. These unique properties allow these films to be used in a variety of applications. These include their use in applications such as energy efficient windows, mostly used in architectural glass [Lew00] burglar alarms [Lew00], electrochromic materials [Wan01b], visual displays [Lew00], and solar cells [Wu99], and even as phosphor powder coatings [Oll02]. The energy efficient window category does not require good electrical properties but rather just a high carrier concentration to achieve a low emmissivity in the infrared region so as to reflect heat. Visual displays are an important application of TCO's. They may be used to dissipate static and absorb magnetic radiation. In the flat-panel display industry, TCO's may be used as a transparent contact for displays that are based on LCD, electroluminescent, and other technologies [Lew00]. In their application for solar cells, they may be deposited on flexible, plastic, substrates at low temperatures in order to avoid damaging the substrate. For this and the application of organic light-emitting diodes (OLED), a lowered deposition has been heavily researched.

Transparent conductive oxides were first discovered in the early part of the 20th century, by Badeker in 1907 for CdO [Bad07]. Since then, the first TCO that gained widespread use was In_2O_3 doped with tin [Cho83], which was developed in the early 1950's and is used in most of the applications that have been developed for TCO's. Other

TCO's that have been discovered include SnO_2 , sometimes doped with fluorine [McM47], Cd_2SnO_4 [McG95], and ZnO [Qiu87]. ZnO has been commonly touted as an inexpensive alternative to ITO for use as a TCO because of its abundance in nature, and thus low relative cost as compared to In_2O_3 [Lew00]. But, this material has been traditionally known for poorer optical and electrical properties as than ITO.

Electronic Properties of Indium Tin Oxide

The origin of the electronic properties of transparent conducting oxides stems from the band structure and doping of these materials. The vast majority of the literature treats TCO's as degenerate semiconducting materials. The term degenerate band structured materials is one that has a wide band gap ($E_g=3.5\text{--}4.3$ eV for ITO) that has the states at the bottom of the conduction band filled through the introduction of substitutional dopants. In the case of ITO, the conduction mechanism in amorphous ITO is the degenerate stoichiometry contributed by oxygen vacancies. It is known that tin does not influence the electrical conductivity of the amorphous indium oxide.

For crystalline indium tin oxide films, the presence of the extrinsic tin doping allowed the contribution of extra electrons to the conduction band, which increases the carrier concentration in the film. Since the carrier is defect and impurity-generated electrons in ITO, the conductivity can be modeled as the product of the carrier concentration and the carrier mobility

$$\sigma = \frac{1}{\rho} = (ne\mu_n + pe\mu_p) \quad (2-7)$$

where n is the concentration of electron carriers (cm^{-3}), p is the concentration of hole carriers (cm^{-3}), e is the electron charge, μ_n is the mobility of the electrons (cm^2/Vs) and μ_p is the mobility of holes.

Following the classical Drude theory of conductivity in metals which is based on equations of motions of electrons, the conductivity can be expressed as

$$\sigma = \frac{ne^2\tau}{m} \quad (2-8)$$

where n is the density of free carriers, τ (sec^{-1}) is the relaxation time for the carrier which relates the time between collisions, and m is the free electron mass. τ relates the motion of the electrons to an applied electric field. The relationship between the mobility and the relaxation time can thus be seen in equation 2-9

$$\mu = \frac{e\tau}{m^*} \quad (2-9)$$

where m^* is the effective mass of the electron. This is a concept that relates the influence of a material on the motions of electrons resulting from applied forces (i.e. electric field). If the relaxation time is constant in a material, a smaller effective electron mass will result in a higher mobility. TCO's tend to have a high effective mass. Typically, the increase in their conductivity is thus due to high carrier concentration. Typically ITO has a carrier concentration on the order of 10^{20} - 10^{21} carriers/ cm^3 . Since changing the effective electron mass of the ITO (this is a material constant) is not possible, it becomes important to produce high-quality ITO films that have a large amount of doping and lower relaxation time. In order to reduce the relaxation time in ITO films, it is necessary to improve the quality of the films, by reducing defects, improving orientation, enhanced crystallinity. The presence of multiple electron scattering mechanisms can drastically effect the carrier mobility of a TCO. These possible scattering mechanisms include the crystalline lattice, ionized impurities, neutral

impurities, and grain boundaries. Equation 2-10 shows the effect of these scattering mechanisms on the total mobility of the film.

$$\frac{1}{\mu} = \frac{1}{\mu_i} + \frac{1}{\mu_a} + \frac{1}{\mu_g} + \frac{1}{\mu_n} + K \quad (2-10)$$

where μ is the overall mobility of the film, μ_a is the scattering due to phonon scattering from charge carrier interaction with the lattice, μ_i and μ_n are the interactions of the carriers with ionized and neutral impurities respectively, and μ_g stems from the interaction of the carriers with grain boundaries. If one scattering mechanism of the culprit for significantly lowered mobility, the overall mobility tends to be near the lowest value.

Phonon scattering through the lattice is an intrinsic part of the material, which occurs though even a perfect crystal. This scattering is temperature dependent and decreases with decreasing temperature. Ionized impurity scattering is typically not considered for the degenerate semiconductor case, which has a near metallic band structure since the ITO is quite heavily doped.

Neutral impurity scattering has been cited as a dominant contributor to scattering that occurs in amorphous ITO. Since Sn is not electrically active in the amorphous state of ITO, it has been argued that SnO_2 clusters act as a neutral scattering sites and thus raise the overall resistivity of the films. Neutral impurity scattering is not a function of temperature but is found to vary with the density of neutral impurities. Increasing concentrations of neutral impurities decrease the mobility of the carriers.

The presence of grain boundaries in the measurement of ITO film resistivity complicates the investigation of the electrical properties of ITO films. Surface states and chemisorbed oxygen can deplete carriers from the conduction band. Surface states can be

formed within a band gap as a result of a break from atomic bonding stoichiometry at the interface. Carriers can enter deep levels and a space-charge region can occur on each side of the grain boundary. In addition, chemisorbed oxygen species at the grain boundary can cause a significant change in the film resistivity. For a larger grain-sized, TCO, the ratio of charge trapped in chemisorbed species to the quantity of total carriers in the grain is small. Thus, chemisorption does not significantly increase resistivity in large-grained material. This may be interpreted as an argument for increased crystallinity in a TCO film.

Optical Properties of Indium Tin Oxide

The optical transparency of indium tin oxide and TCO's in general are generally due to a wide band gap in the optical region usually greater than 3 eV. The optical properties of TCO's arise from the interaction of light with electrons, and the physical structure of the film. In order to increase the optical transparency of the electrons, it is important to minimize these interactions.

Band edge absorption involves absorption of a photon to promote an electron to the conduction band of a semiconductor. This only occurs if the photon energy is greater than the band gap energy of the material. The band gap of ITO ranges from 3.4 eV to 4.3 eV depending on the Burstein-Moss effect (see below) that arises due to extrinsic doping of the film. A band gap of about 3 eV, corresponding to about 400 nm is necessary for transmitting most of the wavelength of the visible spectrum.

The optical band gap can widen due to the introduction of intrinsic or extrinsic dopants. This shift is known as the Burstein-Moss effect. As the carrier concentration increases, the Fermi energy moves above the conduction band edge, resulting in the complete occupation of the states at the bottom of the conduction band. Thus, optically

stimulated transitions to these states can not occur and the optical band gap of the material increases. The amount of band-gap shift is a function of the doping concentration and the density-of-states effective mass (m_{cv}^*). This is shown as

$$\Delta E_g = \frac{h^2}{8 \cdot m_{cv}^*} \cdot \left(\frac{3 \cdot n}{\pi} \right)^{\frac{2}{3}} \quad (2-11)$$

where ΔE_g is the change in band gap, h is the boltzmann constant, n is the carrier concentration.

Another important aspect of the optical properties is the energy at which the plasma absorption edge occurs. Some TCO's, particularly for heat reflection, needs to have the plasma frequency occur in the near-IR region. The plasma frequency of a material is a characteristic frequency of a material, i.e. it is the minimum frequency a photon must have to transmit through the film.

Microstructural Aspects of Indium Tin Oxide

Indium tin oxide has a bixbyite crystal structure that is a c-type rare earth vacancy defect oxide. It has an 80 atom unit cell with the $Ia\bar{3}$ space group and a 1.02 nm lattice parameter in a spacing based on the arrangements of MO_6 coordination groups. This structure is related to the fluorite structure which is a face-centered array of cations with all the tetrahedral interstitial sites occupied by anions. The bixbyite structure is similar except the oxygen positions on the corner of the cube and metal atom at the center of the cube are removed and replaced with units that have missing oxygen in the body or face diagonal. The stacking is such that indium is distributed between indium is distributed in 2 non-equivalent sites with $\frac{1}{4}$ of the indium atoms at the center of a distorted oxygen octahedron and the $\frac{3}{4}$ positioned the center of a more distorted octahedron that forms

from the removal of two oxygen atoms. Paine et al. posit the in the amorphous state is formed during physical vapor deposition processes when these MO_6 coordination units are incorrectly oriented when they are incorporated into the growing film. The restricted mobility of these clusters at low substrate temperature preserves the misorientation of the coordination units and consequent bond distortion.

The first and most important aspect is the influence of substrate temperature on the microstructure of ITO films. ITO has a “crystallization” temperature, which occurs around 150 °C. Most films that are deposited by conventional PVD methods below 150 °C tend to have an amorphous microstructure. Above, 150 °C, the microstructure tends to have a crystalline microstructure that is primarily composed of In_2O_3 as the primary phase. Paine et al. points out that this crystallization coincides, however, with the melting point of In metal (~157 °C) [Pai99]. Since these structures are deposited under thermodynamic conditions that are far from equilibrium, it is difficult to predict the microstructure of these films. Thus, the presence of different phases is primarily determined by empirical evaluation. Yi et al. and Vink et al. [Yi95, Vin95] both report reported partially crystalline microstructures for samples that were deposited around this crystallization temperature.

Morikawa et al. reported for DC-magnetron sputtered ITO thin films the presence of small crystalline nuclei in an amorphous matrix in room-temperature deposited samples [Mor00]. These samples, upon annealing in an oxygen or vacuum ambient, took on a corresponding microstructure that seems to parallel the microstructure of films that were deposited above the crystallization temperature, i.e., blocky grains of In_2O_3 [Adu01].

However, they reported a decrease in electrical resistivity during the vacuum anneal which was attributable to crystallization and activation of Sn ions.

Nakao et al. performed the most comprehensive transmission electron microscopy study of vacuum evaporated ITO and ITO with SnO_2 mixtures to delineate the microstructural characteristics [Nak00]. At low temperatures, they found that amorphous In_2O_3 contained In crystallites. This agrees with the presence of nuclei discussed above and the crystallization temperature occurring around the melting point of In. In pure In_2O_3 films had the microstructure corresponding to those reported above when they were annealed. However, when these films were evaporated and included Sn and SnO_2 , they discovered the presence of an additional phase, which they termed SnO. This additional phase had the crystallographic shear (CS) structure and was formed by a decomposition of SnO_2 or the oxidation of Sn. On a commercial crystalline film with low resistivity, TEM revealed the presence of SnO and In_2O_3 , some of which had a complex twinned structure.

Indium Tin Oxide Thin Film Processing

Indium tin oxide materials have been deposited by a number of techniques. These include sputtering, spray pyrolysis, electron-beam evaporation, and pulsed laser deposition. RF sputtering tends to be the most used physical vapor deposition technique for ITO films. However, for some applications, the energetic sputtered atoms have some limitations, including damage of organic substrate layers by energetic particles. In contrast, pulsed laser deposition has an energy distribution that is thermalized via gas collisions.

Film stoichiometry and materials properties deposited by any method are a strong function of substrate temperature, oxygen partial pressure, and film doping. The influence

of substrate temperature on the microstructure was discussed above. The effects on other properties of these factors will be discussed below.

Substrate temperature influences are the typical influences that one sees in most thin films. For crystalline ITO films, the substrate temperature increase causes film crystallinity to increase [Ben01] and film roughness to decrease [Vin95]. The corresponding electrical and optical properties of these films tend to improve as resistivity decreases and internal stress decreases. Films that undergo an anneal from room temperature into the crystalline region tend to have high internal stress, especially if there are crystalline nuclei present in the surface of the film [Vin95].

Across the amorphous-crystalline transition, it is shown that the resistivity of the films decrease significantly as ITO films crystallize when the films are processed either by changing the substrate temperature for deposition [Adu00] or annealing of amorphous ITO films [Vin95]. Low-temperature crystallization of amorphous indium tin oxide films that were deposited at low temperatures was studied by Paine et al. [Pai99]. By monitoring the resistivity of these films during isothermal anneals around the crystallization temperature, they showed that structural transformation from the amorphous to crystallization underwent a structural relaxation of the amorphous microstructure which changes the ionized vacancy concentration, which in turn, increased the carrier density of the material. When crystallization occurred, the reaction obeyed a classic nucleation and growth with a growth parameter that is consistent with 2-3 dimensional growth. These phase transformations that occurred were measured by monitoring the electrical resistivity during annealing.

The effects of Sn or SnO₂ doping on the electrical and optical properties of the film may be divided into two regimes. First, for amorphous, room temperature deposited films, an increase in the doping concentration leads to an increase of the overall resistivity of the film [Adu02, Adu00, Mor00]. This is significant because it is known that Sn is not electrically active in amorphous ITO films [Izu02] and SnO_x clusters may act as neutral scattering sites.

If samples were either annealed above or deposited above the crystallization temperature, it was apparent that the dopants became electrically active and the film resistivity decreased and the optical properties became more transparent in the visible region. Increased doping tended to increase the resistivity of the films as well as more carriers became active in the films [Adu00, Mor00]. Doping tended to increase the frequency at which plasma absorption took place [Adu02] and moves the reflectance region well into the infrared region. Quaas and Wulff showed by grazing incidence XRD that the lattice constant in the film increased with increasing tin content and a corresponding lowering of resistivity and domain size occurred [Qua98].

Oxygen partial pressure affects the microstructure, electrical and optical properties of ITO films in a complex manner. For low temperature-deposited samples, it may be separated into 3 regimes, i.e., at low partial pressures of oxygen ($pO_2 > 5 \times 10^{-3}$ Torr), medium partial pressures (5×10^{-3} torr $< pO_2 < 1 \times 10^{-2}$ torr) and high pressure ($pO_2 < 1 \times 10^{-2}$ Torr). At low pressures, the film is highly nonstoichiometric. It probably contains free In and Sn and is not well described as an oxide semiconductor. These films are amorphous and optical transmission of these films is poor. At medium partial pressures, there is a tendency during PVD for the ablated species to react with the background gas and deposit

a slightly substoichiometric oxide. This allows good resistivity values since the conduction mechanism in amorphous ITO is due an increase in carrier concentration from oxygen vacancies. At slightly higher pressures, the oxygen vacancies decrease but enhanced mobility occurs because stoichiometric ‘nanocrystal’ clusters occur. In the high partial pressure regime, the gas density is so great that many target species can not reach the sample and thus metal-deficient film forms. [Mor02a, Cra00a, Vin95, Men97]

The effect UV energy on the electrical, optical, and structural properties of ITO has also been discussed by a number of authors. Craciun et al. [Cra00a] showed a marked decrease in resistivity of pulse-laser deposited ITO films by using a Hg lamp to induce improved oxygenation of the films through growth by atomic oxygen. Mori et al. studied the effects of a post-deposition ozone anneal on the opto-electrical properties of the ITO films. It was found that the optical transmittance and the resistivity of the films were improved by a large increment in carrier density due to strong oxidizing ability of the ozone [Mor02b].

Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a complex thin film process whereby a high powered excimer laser strikes a solid bulk ceramic target, with the target material (also called *ablated* material) escaping in the form of a plasma plume and traveling in a vacuum or residual gas ambient towards a substrate. A schematic of a typical PLD system is shown in Figure 2.4. As can be seen from the figure, the target must be rotated, typically at a speed of 1 Hz, so as to ensure uniform erosion of the target during ablation. Usually, the substrate is heated to help in controlling the film properties [Cra00c, Sin98].

Several accessible and important experimental parameters for laser ablation include substrate temperature, laser energy density, relative and absolute arrival rate of the atoms

for compound films, and the pressure in the chamber. The substrate temperature influences the morphology and microstructure of the films, which influences the desired properties of the films. The laser energy density influences whether the target is heated in a surface or bulk manner. This may affect the presence of particles in film, one of the main drawbacks of PLD. The relative arrival rates of the atoms in a compound film determine the chemical composition and variations in composition of the films. Finally, the pressure in the chamber tends to influence the plume shape and size, which influences the deposition rate and kinetic energy of the depositing species. If a reactive gas is employed, such as the deposition of an oxide in the presence of residual oxygen, the growing film may incorporate some of the more volatile species into the growing film and maintain oxygen stoichiometry in the oxide.

PLD has a large number of important advantages that include its versatility in target materials (any material with an optical absorption coefficient $\alpha > 10^5 \text{ cm}^{-1}$ may be easily deposited), low substrate temperature required for high quality films, huge supersaturation ratio, and the stoichiometric transfer of multiple elements in a compound film. Two key disadvantages have limited PLD to being a research tool. One is the presence of particles in the ablated material, which preclude its use as a deposition technique for large-scale manufacturing of electronic or optical materials, which require a high degree of uniformity and quality. The second important disadvantage is a rapidly changing thickness profile in the deposited films, which does not easily allow for consistent coatings.

UV-assisted Pulsed Laser Deposition of Thin Films

Further reduction in the process temperatures of thin films deposited by pulsed laser deposition would be advantageous as it will prevent or at least limit harmful film and/or

ambient gas-substrate interaction, unwanted substrate interdiffusion processes, and re-evaporation of volatile components [Hor91]. To lower the film processing temperature without adversely affecting the film quality, a non-thermal energy source and a more reactive gaseous atmosphere are needed. Ion beam-assisted PLD has been used for the successful growth of several materials [Hol99].

A variation of laser-assisted PLD replaces the second laser that is used to irradiate the substrate with a low pressure Hg lamp, which then creates a reactive atmosphere. This process has been studied in great detail by Craciun et al [Cra00d]. In order to determine the optimal conditions for the deposition of a thin film, the FWHM of a the strongest peak in the film was measured and optimized with regard to the oxygen partial pressure in the system.

The effects of UV irradiation are twofold: firstly, an oxide sample deposited in a oxygen partial ambient experiences the presence of atomic oxygen and ozone since these dissociate at 185 nm and 254 nm, the characteristic wavelength of Hg lamps. Secondly, illumination of the substrate leads to increased adatom mobility, which could lead to enhanced crystallinity in the films.

Craciun et al [Cra00e] showed the low-temperature growth of Y_2O_3 , ZrO_2 , and barium strontium titanate (BST), silicon carbide and ZnO. It was shown that UV PLD films exhibited better structural (i.e. lower FWHM, increased crystallinity for Y_2O_3 films), optical (refractive index values close to bulk values) and improved surface morphology. As well, the presence of physisorbed oxygen in some dielectric films was reduced [How02].

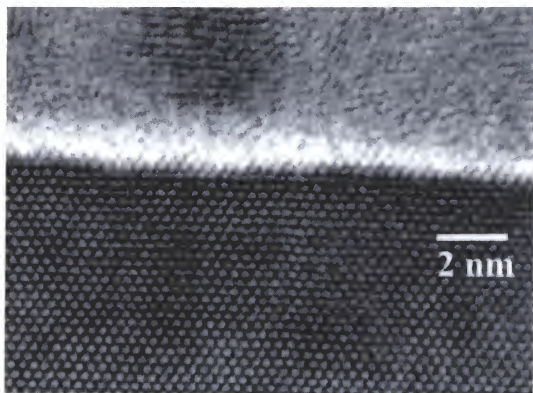


Figure 2.1 HRTEM interfacial layer from an as-deposited zirconia thin film [Ram02]

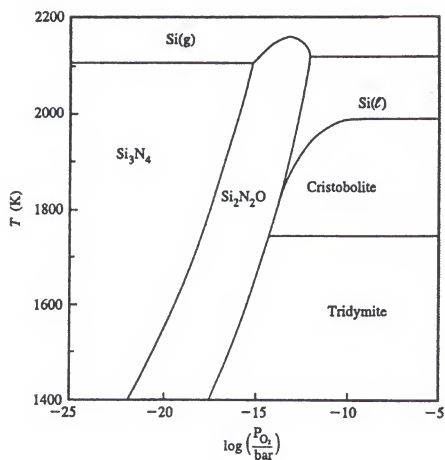


Figure 2.2 Thermodynamic phase diagram of the Si-N-O system [Gus99]

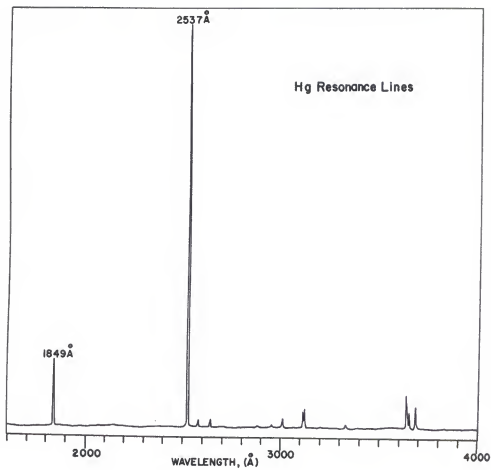


Figure 2.3 Emission spectrum from a low-pressure mercury source [Oka78]

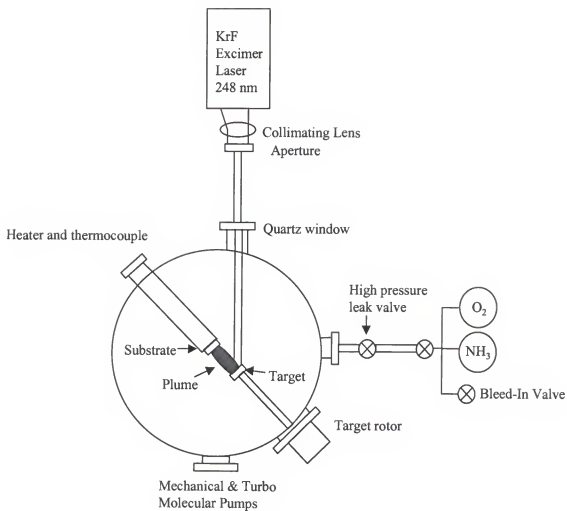


Figure 2.4 Schematic of a typical pulsed laser deposition picture

CHAPTER 3 EXPERIMENTAL PROCEEDURE

Introduction

In this study, several sets of experiments were undertaken in order to examine various aspects of low temperature growth of thin films. The formation mechanisms of various types of oxide and nitride thin films and temperature effects during their deposition were explored. The first experimental section of the study focuses on the low temperature growth of high-k dielectric films such as yttrium oxide (Y_2O_3) and zirconium oxide (ZrO_2), particularly with a focus on interfacial layer formation. The effect of pre deposition processing of these films on the formation of the interface between the substrate and film was also explored. The next experimental set examined the role of UV irradiation in the lowering of the formation temperature of ultra-thin silicon nitride layers. Finally, the third set of experiments explored the in-situ use of UV irradiation during deposition to affect the microstructural properties of indium tin oxide films.

All three sets of films were characterized by a series of techniques. These may be divided into several categories: i) microstructural characterization including transmission electron microscopy, both conventional and high-resolution (TEM and HR-TEM, respectively), x-ray diffraction (XRD), both grazing incidence (GIXD) and conventional theta-2theta geometries, and x-ray reflectivity (XRR), ii) chemical characterization, utilizing x-ray photoelectron spectroscopy (XPS) and iii) optical and electrical property characterization, such as variable angle spectroscopic ellipsometry (VASE), UV/VIS spectrophotometry, capacitance-voltage (CV), current-voltage (IV), and four point probe.

The approach for preparing the film sets will start with a description of the film deposition apparatus, namely the pulsed laser deposition system (PLD) and the excimer lamp system. Then, the specific experimental sets that were prepared will be detailed next and finally the characterization techniques will be described in detail.

Sample Deposition

Film samples were deposited and processed by a number of techniques. These include pulsed laser deposition, in-situ UV-assisted pulsed laser deposition (UVPLD), and UV-lamp photodeposition.

Pulsed Laser Deposition of Thin Films

Thin films of Y_2O_3 , ZrO_2 and Indium Tin Oxide (ITO), were deposited at a variety of temperatures by pulsed laser deposition. Figure 3.1 is a picture of the laser deposition system from the outside. This shows some of the required equipment such as the feedthroughs, the Varian-brand sapphire leak valve and the heater. Figure 3.2 is a picture of the system through the top viewport and shows the target, substrate holder, substrate shield, and the illuminated lamp assembly (see section on photodeposition of nitrides). Typically, chamber pressure was at least on the order of 10^{-6} Torr, which is characterized as high vacuum condition. Most of the films were deposited on silicon wafers, although a few of the samples were deposited on Soda Lime glass (Corning™ glass). Standard silicon substrate sample sizes were about 4 cm square.

A typical film deposition that employed a silicon substrate started with a standard SC-1 cleaning. Some p^{++} doped silicon wafers were used for microstructural evaluation. P-type doped silicon wafers were used for making test capacitor devices for CV and IV measurements. The silicon substrates were rinsed with deionized water, followed by an acetone and methanol rinse, and finally another deionized water rinse. The wafers were

then placed in a solution bath consisting of 40 mL of deionized water, 8 ml of 30% dilute hydrogen peroxide, and 2 mL of ammonium hydroxide at 80 °C for 10 minutes. This cleaning treatment is known as an SC-1 treatment. After this cleaning treatment, the substrate was removed from the bath and rinsed in deionized water.

To remove the native oxide from the silicon wafers, the substrates were placed in a dilute 1 % hydrofluoric acid solution for ten minutes and finally blown dry by ultrapure nitrogen gas.

To attach the samples to the Neocera brand heater, several methods were employed. Most samples were attached by silver paste, which allowed excellent thermal contact with the substrate. Substrates that were to be used for FTIR studies and optical transmittance measurements were attached with a mechanical clamping device so as to preserve transparency on the substrate backside. This apparatus is attached to posts that run parallel to the heater and has an open disk shape so that the plume may reach the substrate. The disk has pins running through it that mechanically affix the silicon or glass substrate to the heater.

The deposition chamber was placed under vacuum, first by a MD4T dry diaphragm pump to the 10^{-2} Torr regime and then by a Varian brand turbopump that was engaged to pump the sample down to a pressure of at least 10^{-6} Torr. A Gramile-Philips convection gauge measured medium pressure ranges, and a Varian ionization gauge measured the high-pressure regime.

The silicon samples were then heated, usually at a ramp rate of 10 degrees per minute. When the sample arrived at the desired temperature, it was held for 10 minutes at the temperature in order to stabilize the temperature on the surface of the substrate. Coming

glass samples were heated at a rate of 7 degrees per minute. For depositions with temperatures that were higher than 500 °C, an optical pyrometer was used to verify the temperature on the surface of the sample and the heater temperatures as measured by a thermocouple (Omega K-type). Subsequently, the heater temperature was adjusted so that the pyrometer registered the desired deposition temperature. For lower temperature depositions that required the mechanical clamping apparatus, a calibration was performed by attaching a thermocouple to the surface of the sample and comparing the actual surface temperature to the heater temperature. This calibration curve may be seen in Figure 3.3 for both silicon and coming glass substrates.

Once the sample has reached the deposition temperature, cooling water to the laser (Lambda Physik, wavelength = 248 nm) was started and the laser was turned on. After a warm-up period of at least 10 minutes, operational software was started to control the laser fluence, repetition rate, and deposition duration. Several test pulses were fired with the aperture closed while monitoring the laser energy to establish that the laser energy was stable. After this warm-up, the laser was fired into the chamber to get the rotating target clean of any contamination layer that may have formed on the target when it was exposed to the atmosphere. The substrate is shielded during this preconditioning to prevent any unwanted deposition.

When the temperature, laser, and target were stabilized, any residual ambient gas desired for the experiment was introduced. This is performed using a sapphire bleed valve, which allows fine control of the pressure inside the deposition chamber. The target shield was then uncovered and the substrate exposed to the plasma plume. The substrate to target distance is approximately 11.5 cm for the depositions performed in this

dissertation. The laser was then engaged and the film deposition performed. Depending on the desired ambient, the gate valve to the pumps was closed and gas was introduced for post-depositions anneal during cooldown. After the sample cooled, it was removed from the chamber with plastic tweezers to prevent surface contamination for characterization.

In-situ Ultraviolet-Assisted Laser Deposition using Mercury Lamps

Some samples were deposited under UV illumination by low-pressure mercury (Hg) lamps, which emit UV radiation at wavelengths of 185 nm and 254 nm. These lamps were placed in a special rack between the substrate and target with two lamps above and two lamps below the target. The mean distance of the lamps to the substrate is approximately 9 cm. The lamps were ignited under vacuum during the sample heating for approximately 2 minutes while the sample was heating in order to warm up the lamps and obtain a consistent distribution of ionized mercury vapors within the lamps and thus obtain uniform illumination. After the lamps were warmed up, they were ready to ignite during a deposition. When the sample was ready for deposition (i.e. laser, target and substrate stabilized), the lamps were ignited prior to laser deposition. Typically, they were left on during laser deposition through the post-deposition annealing stage. The energy of each mercury lamp was measured using a Ushio energy meter and had an energy density of 50 mW/cm^2 .

Mercury Lamp Nitride Photodeposition

Some of the photodeposited samples were processed using mercury lamps without any laser deposition, primarily for the pre-nitridation step in some of the nitridation experiments. The mercury lamp deposition experiments were performed by introducing ammonia gas into the chamber after the sample reached the desired temperature and the

lamps were turned on. Such experimental variables as ammonia pressure, lamp power, chamber, temperature, and deposition time were explored.

Experimental Design

High K Dielectric Interfacial Layer Experiments

As mentioned in the previous chapter, the presence of an interfacial layer between a deposited dielectric film and a silicon substrate has been observed in many dielectric candidate systems. The nature of this interface was an important aspect to study. First, the precise nature of its composition was important to explore. In order to determine the nature of this interface, it was necessary to deposit a series of samples and vary some of the important film parameters, such as thickness. This may show the evolution of the interfacial layer composition with time and cast light on the evolution of the film at its earliest growth stages.

For these experiments, 1 inch high purity (99.99%) Y_2O_3 and ZrO_2 targets (purchased from Kurt J. Lesker, Inc.) were ablated at the optimum conditions (600 °C and 10 mTorr) that were found for these materials from the literature [Cra00b] onto silicon substrates. All samples were deposited with a fluence of 1 J/cm^2 and at a repetition rate of 5 Hz. The thickness of these films were varied from 20 Å to 80 Å. By changing the thickness of the films, some of the transport mechanisms that occur as the film grows may be explored.

Next, several experiments were designed to examine suppression of the formation of the interfacial layer. These include a series of high-temperature pre-deposition hydrogen anneals in order to clean the silicon surface of any residual oxygen that was present on the surface of the film. Another elaborate series of pre-surface nitridation experiments were performed to build a monolayer thick diffusion barrier for the formation of the interfacial layer. Hydrogen pretreatments were performed at 850 °C for 2 minutes and 10

Torr using ultrapure hydrogen (99.999%) prior to a film deposition at 600 °C and 10 mTorr of O₂. For some of these experiments, the residual oxygen pressure was lowered to .01 mTorr to examine the relationship between hydrogen passivation of the surface and oxygen pressure in the formation of the interfacial layer.

These samples were then characterized to determine whether the nitride layer aided in the suppression of interfacial layer formation during subsequent film growth. Some of the films deposited on pre-nitrided samples were annealed under an oxygen ambient to determine whether the nitride demonstrated diffusion barrier capabilities.

Mercury and Excimer Lamp Experiments

In order to optimize the thermal budget of the pre-nitridation processing, a series of nitridation experiments were undertaken to determine the effect of UV-illumination on lowering the silicon nitridation temperature. These experiments were undertaken by introducing ammonia gas into the deposition chamber when a silicon sample had reached photodeposition temperature, and allowing a gas-phase reaction to occur with the silicon surface. Experimental parameters that were varied include nitridation time (1 min to 1 hour), ammonia pressure (0.1 Torr to 100 Torr), and type of exposure intensity to UV illumination (mercury-based). These samples were characterized by XRR, VASE, and XPS.

In-situ UVPLD

A series of experiments was performed to examine the effect of non-thermal UV radiation on the microstructure and properties of indium tin oxide thin films during PLD. These experiments were undertaken at a variety of deposition temperatures from room temperature up to 180 °C. This material system was selected, as opposed to the previously studied high-k dielectrics, because, as previously mentioned, transparent conducting

oxides are suitable candidates for low temperature deposition onto specialized substrates. Since indium tin oxide has a low crystallization temperature ($T \sim 150^{\circ}\text{C}$), it may show a dramatic effect on the microstructure of the films due to UV illumination.

ITO thin films were grown using a 10 at% SnO_2 -90% In_2O_3 target to a thickness of approximately $900\text{\AA}$ under an oxygen ambient of 10mTorr on both glass and silicon substrates. The effects of UV illumination during deposition on film microstructure, optical, and electrical properties were characterized and related to the oxygen stoichiometry of the film.

Film Characterization

Microstructural Characterization

The two primary microstructural characterization techniques that were utilized include transmission electron microscopy and x-ray diffraction. These techniques will be described below.

Transmission Electron Microscopy

TEM was used frequently in this investigation in order to measure a number of microstructural parameters. These include grain size, texturing, interfacial layer thickness and roughness, and phase type and distribution.

The basic principles of TEM lie in the interaction of a very thin sample (less than 200 nm) with a high energy ($\sim 100\text{ keV}$ or above) electron beam, which transmits through the sample. Based on the interaction of this beam with the sample, an extremely high magnification (on the order of 10^6 times), diffraction information (phase type and defect structure) and chemical information are available for examination [Wil96, Sic92].

Conventional TEM (i.e. using diffraction contrast mechanisms) was performed routinely, specifically on plan-view (i.e. viewing the film through its thickness) samples,

in which the grain structure, phase type, crystallinity, and texturing was examined. A Philips 420 electron microscope operated at 120 keV was used for plan view imaging of thin films deposited on silicon. The primary operation mode for this TEM was in bright-field and selected area diffraction mode.

All specimen preparation is focussed on producing a very thin area so that the electron beam may transmit through the sample. Plan view sample preparation began with the use of an ultrasonic coring drill (Gatan Model) to bore out a 2.8 mm disk from a coated substrate. Once this disk was cut out, the sample was mechanically polished from the back side (with the film side protected) to a thickness of approximately 80 μm . The samples were then prepared in one of two possible ways: etching or ion milling.

For the plan view etching of the samples, they were attached, film side down, using paraffin wax to a teflon square, which was resistant to the hydrofluoric acid used in the etchant. The wax was spread around the perimeter of a sample, leaving an exposed hole of approximately 2 mm, to hold the sample down and ensure that etching reagent did not penetrate the film side. Then, the exposed side was held under a slow drip of acid solution (75% nitric acid to etch and oxidize silicon, 25% HF to etch silicon oxide) until the sample was penetrated through the film side. Since silicon transmits red to orange light when it has a thickness under 10 μm , this color change was a good indicator of near sample penetration. The perforated sample was then thoroughly rinsed in deionized water to remove any particles and all of the etchant.

After the sample was penetrated, it was placed in a bath of trichloroethylene to dissolve the paraffin wax overnight. The samples were then rinsed in methanol and deionized water, dried and examined in the TEM.

Samples that were prepared mechanically were dimpled (Gatan Model 656 Dimple Grinder) using a copper wheel to a depth of approximately 7 μm followed by a finer polish to a depth less than 5 μm . The final thinning process was performed in a Gatan shallow angle ion mill (Precision Ion Polishing System Model 691), which uses Ar^+ ions to sputter the sample to electron transparency. As soon as a hole was visible in the samples, they were ready for examination.

Cross-sectional HR-TEM was performed in order to get an idea of film thickness, roughness and interfacial layer thickness. Since these parameters are easily determined upon inspection under high-resolution conditions, they were used to adjust and guide the modeling of XRR spectra and to help in interpreting XPS data.

Sample preparation for cross-sections required first a gluing of the pieces of the substrate together face to face, accompanied by dummy silicon wafers that allow the total sample to reach the required diameter of 2.8 mm required for TEM samples. These wafers were glued using Gatan G-bond epoxy or M-bond epoxy and cured at a 100 C temperature on a hot plate while being clamped together to ensure thin glue lines at the wafer/wafer interface. This sample "sandwich" was then sliced using a diamond wafering blade into small 1 mm slivers and thinned using silicon carbide polishing papers. The slivers were then cored using the ultrasonic drill, making certain that the interface of interest was at the center of the cored disk.

The disks were mounted on a glass stub and one side was ground to a rough polish with 1200 grit silicon carbide polishing papers and then slightly dimpled using first a 1 μm diamond paste with a felt polishing wheel and .05 μm alumina paste with a different polishing wheel. This step is important so that the surface roughness of the sample is

ready so that when the sample is flipped over for grinding and polishing to ultimate thickness, the sample may transmit the dimple backlight and give an accurate measure of the thickness of the sample. The cored disks were then flipped over thinned using silicon carbide papers ranging from 240 to 1200 grit to a thickness of about 90 μm , at which point they were dimpled to a thickness of 10 μm using a balanced and extremely even brass wheel. They are then polished to a thickness of 5 μm (or to the point in which the silicon appears yellow when light is transmitted through it). It was extremely important to obtain a very thin sample before insertion in the ion mill to reduce milling time.

The samples were then inserted into the PIPS ion mill system and milled at a 4-degree shallow angle from the top and bottom of the samples. The samples were inserted slightly off center so that the initial perforation of the sample was in the center of the substrate piece upon which the thin film was deposited. The ion guns were then lowered to a shallower angle of 3 degrees each and the ion beam energy was lowered to 3 keV to slowly grow the perforated hole to the interface. When the hole reached the interface, the sample was removed from the mill and tested in previewed in the Philips 420C TEM to obtain a rough estimate whether the samples were thin enough for high-resolution work.

Several microscopes were used for high-resolution TEM: a JEOL 4000CX and a JEOL 2010F (F denotes a field emission gun). Before insertion into the 2010F microscope, the samples were plasma cleaned for 1 min in order to remove any stray contamination on the surface of the sample and to preserve good vacuum conditions. After the interface was found, the samples were tilted to a $\{110\}$ zone axis and imaged in high-resolution mode. Energy dispersive spectroscopy (EDS) was also available to evaluate the composition of the interfacial layer and the film.

X-Ray Diffraction

X-ray diffraction (XRD) is a powerful technique for analyzing the microstructure of a sample. XRD has the ability to uniquely identify the crystal structure of various phases in the films, as well as give some qualitative and quantitative evaluation of grain size and preferred orientation of thin films [Cul78, Ton92].

A Philips X'Pert XRD system was used to perform x-ray analysis of the samples. It was operated at 45 keV and 40 mA settings with Cu K α (wavelength = 1.5405 Å) radiation with a 1/8° divergence slit for grazing incidence geometry and 1/2° divergence slit geometry for conventional θ -2 θ geometry. Ultrathin films (<200 Å) were evaluated in the grazing incidence geometry, in which the samples were positioned with the incoming beam taking an extremely shallow angle (slightly greater than the critical angle, at which total external reflection of the X-rays occurs) while the detector sweeps a large angular range. When the signal satisfies the Bragg conditions, a peak from the sample is observed. X-rays only penetrate 100 Å into the sample, thus allowing a large fraction of the diffraction information to be contributed by the film and a much smaller substrate peak as compared to conventional θ -2 θ geometry. Structural information is obtained about atomic planes that tilted parallel to the surface.

The optical setup required to obtain GIXD data includes a specially designed x-ray tube that allows a high intensity x-ray beam with a very small divergence (0.003°). This is an important component since a lot of intensity is required to obtain structural information from an extremely thin layer as in these ultrathin films. Very fine control of angular movement of the source and detector during a scan and a thin-film collimator are also required to obtain an accurate GIXD scan. To acquire a GIXD scan, it was first

important to bisect the beam with the sample to ensure fine alignment. Then, a series of scans at different incidence angles were taken.

For some of the thicker films, a theta-2 theta geometry, in which the sample and detector move in concert while maintaining the same relationship between the incidence and diffracted angle, was performed. Crystallinity evaluation was possible through examination of the full-width at half maximum (FWHM) for some thicker films.

X-ray Reflectivity

XRR is one of the most-used techniques in this study because of the wealth of information that may be obtained about a thin film and found in a non-destructive manner. XRR may be used to measure the thickness, density, and interfacial roughness of single or stacked films (as would be the case of a film on top of an interfacial layer). The rarity of the use of x-ray reflectivity to analyze thin film structures warrants a slightly more involved description, as compared to the previously discussed TEM and XRD techniques.

XRR is based on specular x-ray scattering [Cha97]. Specular scattering occurs when incident and reflected angles of the x-ray signal are equal and the K vector, which is defined as the difference between the incident and reflected wave vectors is perpendicular to the surface. If this $K_{\perp}$ is large, the length scales that are explored are on the order of atomic spacings. However, at extremely shallow angles, the $K_{\perp}$ is small, and length scales larger than atomic dimensions are probed. Then, the x-rays may be treated by the optical formalism, using the equation for the Fresnel coefficients. Figure 3.4 is a schematic [Cha97] that shows the optical setup required for X-ray reflectivity.

Deriving from Snell's law, an X-ray wave passing into a material will be refracted with an angle larger than the angle of incidence. Thus, there is a critical angle for total external reflection. This angle is a good measure of the electron density of the film, which may be correlated with the physical film density.

When the reflected x-ray beam interacts with another reflected beam from a buried interface, the second interface gives interference fringes with spacing between maxima proportional to $2\pi/d$, where d is the film thickness. The amplitude of the oscillation is also dependent on the density difference between the film and the substrate. Surface roughness tends to cause a decrease in the slope of the reflectivity curve at a high incidence angle or K value. An example of a typical XRR curve is given in figure 3.5, which qualitatively shows the features that are indicative of materials properties: thickness, density and roughness.

Acquisition of an XRR spectrum typically requires attaching of the sample onto the X'Pert system holder and changing the optical setup to incorporate a high quality x-ray mirror, line source optics, and a collimating receiving slit and a nickel beam attenuator. A $1/32^\circ$ divergence slit is placed in front of the source to limit most divergence from the x-ray beam to obtain only specular scattering. Next, the sample is aligned so that the film is bisected by the surface of the sample and then the height and tilt of the sample are optimized. Sometimes, a 4 mm mask was placed in front of the incident beam to ensure that the beam struck the most uniform part of the film. Sample acquisition typically took about two hours.

Simulation of film thickness, density and roughness parameters was performed using the Philips software package, WinGixa™. This package allows modeling of actual

reflectivity data to an input model, which calculated a simulated spectrum using the Fresnel optical coefficients. In order to obtain a proper fit of the data, several steps were required. Firstly, some machine parameters, such as the divergence of the beam and the background value (at which signal noise plays a significant role in the goodness of fit) must be inserted. Since this software did not simulate a normalized reflectivity measurement, but rather a profile of the intensity vs. ω , it was important to match the value of the simulated reflectivity spectrum at maximum intensity just before the critical angle to the actual value obtained from the X'Pert.

After these parameters had been inserted, it was then possible to simulate the thickness, roughness and density characteristics of the sample. This started with the insertion of a substrate material with a baseline roughness and then followed with a simulated interfacial layer and then the film layer, with guess values for the thickness and roughness. In order to first determine the density of the film, it was important to focus on the critical angle to determine the density of the uppermost layer, which, at a shallow angle, has the most pronounced effect on the critical angle position. After a first order approximation for the film density was obtained, then the next focus is on obtaining a thickness that matches the oscillations within the spectrum. Finally, the roughness was modeled for each layer to obtain a good match of the reflectivity slope decay. Sometimes, it was necessary to use an additional layer at the surface of the film to account for some contamination that may have occurred on the surface. This layer was usually inserted to fine-tune the critical angle information and usually was confined to having a 5-15 Å thickness and a density typically lower than the density of the film. Starting density estimates for the important materials that were used for modeling the data are listed in

table 3-1 [Lid97], which is shown below. These values are values for materials in their bulk forms. In some cases, however, density values for silicon oxide and silicon nitride measured by x-ray reflectivity measurements [San01] may range from 1.94 g/cm³ to 2.20 g/cm³ and 2.78 g/cm³ to 3.01 g/cm³.

Table 3.1 Typical bulk density values for materials used in X-ray reflectivity modeling.

Material	Chemical Symbol	Density (g/cm ³)
Silicon	Si	2.32
Silicon Dioxide (vitreous)	SiO ₂	1.94-2.20
Silicon Oxynitride	SiO _x N _y	2.78-3.01
Silicon Nitride	Si ₃ N ₄	3.17
Yttrium Oxide	Y ₂ O ₃	5.03
Zirconium Oxide	ZrO ₂	5.68
Indium Oxide	In ₂ O ₃	7.18

Several assumptions were made to facilitate X-ray reflectivity modeling. These include the presence of an interfacial layer (which is confirmed by HR-TEM). If the interfacial layer has a density value between the film and the substrate, it was assumed that this was evidence of some interfacial reaction between the substrate and deposited film. The last assumption was that the deposited film density could not be higher than the bulk values listed above.

Typically, the reflectivity spectra were modeled to a level of goodness of fit that is denoted by a value of χ^2 , which is a measure of deviation from the actual data, took on a value on the order of magnitude of 10^{-1} or less. As well, the ability of the fit to directly model the subtle nuances of the reflectivity curve was an important aspect to accepting the data as usable.

Chemical Characterization

Chemical characterization was primarily performed by x-ray photoelectron spectroscopy (XPS), which allowed the measurement of chemical bonding in ultrathin films and could be used quantitatively to measure the thickness and chemical content of a film.

XPS is one of the most versatile tools for characterizing ultrathin films. It was used extensively in this study, mostly for the exploration of interfacial layers and ultrathin nitride films. Because of the physics that govern the photoelectric effect, it is extremely sensitive to the top two monolayers of a film through to about 100 Å, depending on the attenuation due to the interaction of the film material with the photoelectron. XPS may determine the chemical state of the atoms that are being studied, and then angle-resolved mode, can study buried interfaces. As well, it may be used to determine the thickness of ultrathin films.

XPS is based on the principle that when a photon of sufficiently short wavelength, or high energy, interacts with an atom, it may ionize it and produce a free electron. The kinetic energy, KE, of this electron depends on the energy of the incoming photon (controlled by the Mg K α anode with an energy of 1256.6 eV) and the binding energy, BE, of an electron to the atom in question. The Einstein photoelectric law relates these quantities:

$$KE = h\nu - BE \quad (3-1)$$

where $h\nu$ is the energy of the photon.

The binding energy for each electron orbital is unique for each atom because the electrons are bound to the nucleus by electrostatic attraction and this is different for each type of atom (i.e. a different number of protons in each atomic nucleus). Thus, the

binding energy may be used as a signature energy to identify an atom. A characteristic energy level may be measured for each type of electron orbital that is present in the atom.

Electrons that are closely bound to the nucleus are called core-level electrons. Although these electrons are not involved in chemical bonding with other atoms, they do experience chemical shifts in energy based on their bonding. Generally, as an atom has an increasing charge upon it, its binding energy increases. This binding energy shift allows an accurate measurement of the oxidation states. Characteristic binding energy values for the elements, the literature values for their various valences, and the sensitivity factor, s , which allows comparisons of relative element peaks for stoichiometry comparisons, are listed in Table 3.2. These values are obtained from the Handbook of Photoelectron Spectroscopy [Mou97]. The inelastic mean free path length, λ_e , which determines quantitatively how surface sensitive that element is (see below) for some of the important types of films that are explored in these experiments are listed in Table 3.3.

Table 3.2 XPS values and inelastic mean free path values used in this study.

Element	Compound Stoichiometry	Orbital	Oxidation State	Energy (eV)	Sensitivity factor, s
Silicon	Silicon	2p	Si ⁰	99.5	0.339
	Interfacial SiO _x	2p	Si ¹⁺		
	Silicon Oxide	2p	Si ⁴⁺	103.3	
	Silicon Nitride	2p		101.8	
Carbon		1s	C	284.5	
Nitrogen	Silicon Nitride	1s	N ³⁺	397.4	0.477
Oxygen	Silicon Dioxide	1s	O ²⁺	533.0	0.711
Yttrium	Yttrium Oxide	3d	Y ³⁺	156.0	2.175
Zirconium	Zirconium Oxide	3d	Zr ²⁺	178.9	2.576

Table 3.3 Inelastic Mean Free Path values for silicon oxide and silicon nitride thin films.

Compound	Inelastic Mean Free Path, λ_e (nm)	Reference
Silicon Dioxide	2.96	[Lu97]
Silicon Nitride	1.70	[Che01]

The surface sensitivity of XPS allows the thickness measurement of ultrathin layers (<100 Å). For simple silicon oxide films, the thickness is determined by the Si 2p core level intensity ratio of the oxidized silicon film, I_{oxy} and substrate silicon, I_{Si} by the equation

$$d_{oxy} = \lambda_{oxy} \sin \alpha \ln [I_{oxy} / (\beta I_{Si}) + 1] \quad (3-2)$$

where λ_{oxy} is photoelectron inelastic mean free path in the oxide film, α is a photoelectron take-off angle and

$$\beta = \frac{I_{oxy,\infty}}{I_{Si,\infty}} \quad (3-3)$$

measured on photoelectron opaque films >15 nm at $\alpha > 70^\circ$. This equation is derived based on the assumption that the photoelectron signal has an exponential depth distribution function.

Lu, McCaffrey et al. published a series of the measurements of the XPS photoelectron attenuation lengths based on the above equation by comparing the measured thickness with cross-sectional TEM imaging [Lu97]. These are listed in the table above for silicon and silicon oxide. Chen, Landheer et al. were able to deconvolute the relative signals of the oxygen and nitrogen in an ultrathin oxynitride in order to determine an electron attenuation length for the nitrated portion of silicon oxynitride [Che01]. They also determined the photoelectron attenuation length from a bulk silicon nitride film to be 1.7 nm.

Stoichiometry of a simple mixed-element (i.e. assuming homogeneous composition throughout the film) is also determinable through an analysis of the peak intensities analyzed by XPS. The equation that determines the atomic percent concentration, A_x , of element x within an n -component film was performed using the equation,

$$A_x = \frac{\frac{I_x}{S_x}}{\sum_{x=1}^n \frac{I_x}{S_x}} 100 \quad (3-4)$$

where I_x is the total integrated area for the element being examined. For the case of nitrogen, for example, the area under the N 1s peak would be examined. The integrated area of the oxidized silicon peak would be used to measure the silicon composition of the film. Of course, this model does not take into account inhomogeneities in the film, which include isolation of one element to the interface.

Angle resolved XPS is a useful tool for examining the segregation of certain elements to the silicon/film interface. For ultrathin films, the take-off angle, α , between the sample and the detector, shown schematically in figure 3.6, can be modified so that the signal can be attenuated to sample the surface of the film (at shallow angles) or the bulk of the film, (at high angles). By examining the change in peak intensity for XPS peaks at different angles, one may determine whether certain elements are buried at the interface or are present at the top of the film. An example of this is shown in figure 3.7 for the silicon 2p peak.

Using a Perkin-Elmer PHI 5100 ESCA System operated with a Mg K α (1253.6 eV at 300 watts), ultrathin films were characterized by XPS. All peak values were referenced relative to the adventitious carbon 1s peak of 284.6 eV and shifted accordingly. Some of the high-k dielectric films were examined to determine the role of silicon transport during interfacial reaction. Typically, these samples were examined by angle resolved XPS. Other times, XPS was used to evaluate the thickness of ultrathin silicon oxynitride films that were not measurable by any other technique. Also, a direct measurement of percentage nitrogen incorporation into these films was possible.

Optical and Electrical Property Characterization

Several techniques were used for characterizing the optical and electrical properties of these films. Variable angle spectroscopic ellipsometry (VASE) was used to measure thickness, refractive index and extinction coefficient in these films, UV/VIS spectrophotometry was used to measure film transparency, capacitance-voltage (CV) and current-voltage (IV) were used to measure dielectric properties of some films, and four-point probe methods were used to measure film resistivity for ITO films.

Variable Angle Spectroscopic Ellipsometry

Variable angle spectroscopic ellipsometry (VASE) is a technique that may be used to measure film thickness as well as film optical constants, such as refractive index and extinction coefficient. Ellipsometry measures the change in polarization of a collimated polarized light after it is reflected off of a film surface [Woo92]. The angle that the light makes to the sample normal is adjusted to maximize the sensitivity and accuracy. Ellipsometry is sensitive to films that are a monolayer in thickness, but typically are used to measure the thickness of films on the order of 1 nm to 1000 nm. Since the lateral resolution of ellipsometry is on the order of millimeters, film thickness variations from PLD films may cause some error. In this case, an aperture may be inserted in front of the incident beam in order to adjust beam size. However, this aperture may cause a loss of signal.

Since light is an electromagnetic wave, it has an associated electric field (E) that may be divided into x-vector and y-vector components. With a beam of out-of-phase polarized light, the electric field in each direction traces out an ellipse, which describes the polarization state of the light. Ellipsometry determines the azimuthal angle of the electric field vector along the major axis of the ellipse relative to a given plane of reference and the ellipticity, which is the ratio of the longest/shortest side of the ellipse.

As in XRR, a spectrum over a variation of wavelengths may be recorded and the results modeled through the use of Snell's law and the Fresnel reflection coefficients. Usually, the experimental polarization data must be modeled and compared to the spectra that would be derived from an assumed structure, i.e. some structure that has a substrate, interfacial roughness, film area, and surface roughness. In this case a regression analysis must be used to determine the system's physical parameters. By minimizing the error

between experimental and modeled data, one may refine the experimental model. However, in some complex films, there are optical constant unknowns as well as thickness unknowns. Thus, there may be many solutions for the same experimental data.

Because of the challenges of ellipsometry, most of the modeling of the experimental VASE data relied on the use of experimentally determined parameters such as thickness and roughness from XRR. After using these values, optical constant data may be determined for these samples.

VASE experiments were acquired with a Woollam EC110 Ellipsometer at an incident angle of 70° . The system was first aligned using the accompanying instrument WVASE software and then calibrated using a known SiO_2 thermal oxide sample. After the calibration, thin film samples were aligned and spectroscopic scans were acquired. A theoretical guess model was inserted into the regression software and a model was generated and fit to the experimental data. Optical constants and thickness were then determined.

UV/VIS Spectrophotometry

UV/VIS spectrometry was used to measure the optical transmittance of indium tin oxide films. A Perkin-Elmer Lambda 800 UV/VIS spectrometer was used with a double beam configuration. The wavelengths that were scanned ranged from 200 nm to 800 nm. The percent transmittance was plotted relative to the wavelength. A blank Corning glass substrate was inserted as a reference sample and this background was subtracted from the transmittance measurements for the sample that a film deposited on the surface. Samples were typically measured with a 1 nm/sec resolution.

Capacitance Voltage and Current Voltage Measurements

Capacitance-voltage and current-voltage measurements were performed on a series of samples in order to determine the electrical characteristics of some of the dielectric layers that were processed. High-K dielectric films were first deposited by PLD on to p-type silicon wafers and then simple capacitor structures were made either by thermally evaporating gold dot structures on to the surface or by platinum sputtering through a metallic mask. Backside wafer contacts were deposited either by gold evaporation or by coating the backsides with silver paste. Measurements were typically performed on gold dot circles that had a diameter of $8 \times 10^{-6} \text{ m}^2$.

A Keithley 590 CV Analyzer was used to measure the capacitance from -3 to 3 V since the devices are on p-type wafers. A C-V bias sweeping technique was employed that ensured that sample was independent of electron-hole pair generation time in the silicon wafer. The samples were first biased at the inversion voltage, which would cause deep depletion. Then, the sample was illuminated for a few seconds and then left in darkness. This would cause the generation of electron-hole pairs much faster than depletion and allow a stable inversion region to be formed. Then the samples were measured for C-V characteristics.

The capacitance of the structures was plotted relative to the bias voltage and from this, and using other data for sample thickness, the dielectric constant of the film could be easily determined following the equation,

$$k = \frac{Ct}{A\epsilon_0} \quad (3-5)$$

where C is the capacitance of the film in accumulation, t is the thickness of the film, A is the area of the capacitor structure and ϵ_0 is the permeability of free space and is equal

to 8.85×10^{-14} F/m. As was written in equation 2-1, the equivalent oxide thickness could also be calculated. Finally, the dielectric constant of the interfacial layer could also be determined using the equation

$$\frac{1}{C_{tot}} = \frac{1}{C_{film}} + \frac{1}{C_{int}} \quad (3-6)$$

where C_{tot} is the overall capacitance of the film and interface, C_{film} is the capacitance of the film and C_{int} is the capacitance of the interfacial layer. From this analysis, dielectric constant of the interfacial layer can be determined as

$$K_{int} = \frac{K_{tot} K_{film}}{K_{tot} t_{film} - K_{film} t_{tot}} t_{int} \quad (3-7)$$

where the subscripts int, film and tot denote interfacial layer, film layer and total combined layer. Using this equation and assuming literature values for the deposited film and determining the thickness from other techniques, the dielectric constant of the interfacial layer could be calculated.

A Keithley 236 SMU Current-voltage apparatus was used to determine the current-voltage characteristics. Again, the measurement was performed from inversion to accumulation voltages (-3V to 3 V).

Four Point Probe Measurements

Four-point probe measurement is a convenient way to measure the sheet resistance of a thin film. First, one lightly presses a four-point metal-tip probe assembly onto the surface of the film. Then, the outer probes are connected to a current source and the inner probes detect a voltage drop. By applying an input current (in the case of ITO at near 10

nm thickness, 1 mA) through the film through, the voltage was measured and the sheet resistance, R_s was determined by the equation,

$$R_s = \frac{KV}{I} \quad (3-8)$$

where K is a constant depending on the configuration and spacing of the contacts, I is the input current and V is the corresponding measured voltage [Ohr92]. Typically, the value of K is 4.53 if the probe spacing is large relative to the film thickness. The resistivity of the films was then determined as

$$\rho = R_s t_{\text{film}} \quad (3-9)$$

where t_{film} is the thickness of the film.

A Jandel Multi-Height 4-point probe connected with a Keithley 2010 multimeter was used to measure the sheet resistance of the indium tin oxide films deposited on Corning glass.

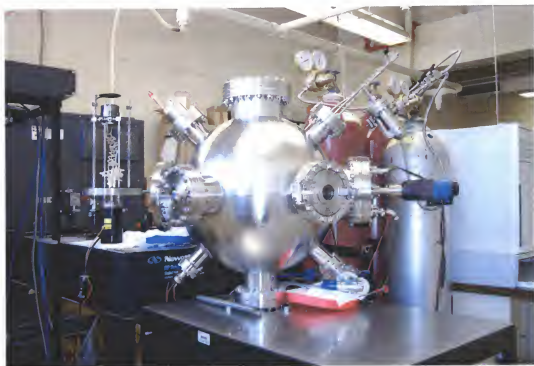


Figure 3.1 Pulsed laser deposition system



Figure 3.2 Top view look at pulsed laser deposition chamber, with in-situ lamps illuminated.

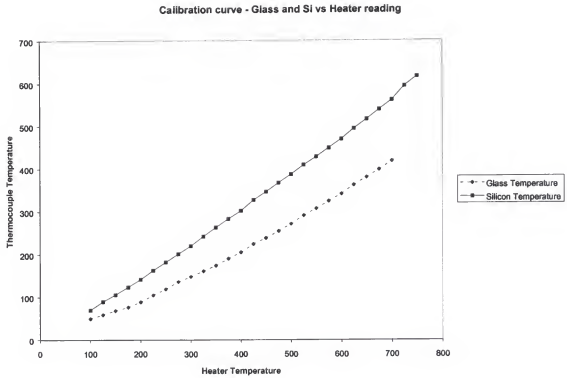


Figure 3.3 Calibration curve comparing thermocouple at surface of the substrate with the heater temperature

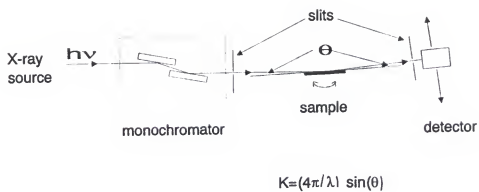


Figure 3.4 Schematic optical setup of a reflectivity measurement system [Cha970].

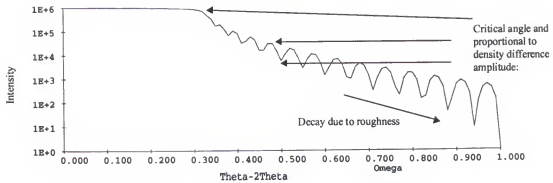


Figure 3.5 Typical XRR reflectivity curve showing the how materials properties affect the XRR spectrum.

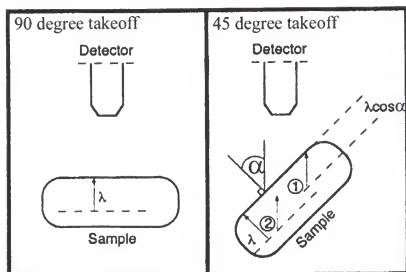


Figure 3.6 Experimental schematic of the detector/sample take-off angle, α , showing that deep regions in the tilted sample are less likely to be detected

Si 2p

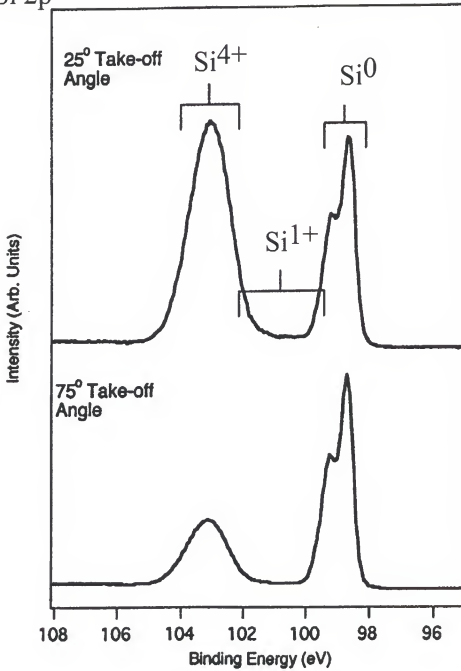


Figure 3.7 Typical XPS spectrum from the silicon 2p region showing the effect of angle on the attenuation of the oxidized silicon signals as a function of take-off angle.

CHAPTER 4 RESULTS AND DISCUSSION

Interfacial Layer Formation Mechanism

The presence of an amorphous interfacial layer can be seen in Figure 4.1, which is an HR-XTEM micrograph taken from a Y_2O_3 film. As can be seen from the figure, the thickness of the interfacial SiO_x layer is about 20 Å. This layer was labeled SiO_x . It can be seen from the micrograph that the interfacial layer/ Y_2O_3 interface a roughness on the order of 4-6Å, which may be indicative of mixing between the interfacial layer and the Y_2O_3 film.

It may be argued that the interfacial growth before deposition is due to the presence of a thermal oxide that forms from a low partial pressure of oxygen in the high vacuum chamber before deposition as the oxide film is heated. Figure 4.2 show high resolution XPS scans of the Si 2p region recorded from an as-cleaned, hydrogen-passivated Si sample and a cleaned Si sample that was heated in vacuum, held at 500 °C for 30 min in partial pressure of 10 mTorr and cleaned. Figure 4.3 shows the Si 2p region from a sample that had a very thin ~ 40 Å Y_2O_3 layer deposited at 275 °C and 10 mTorr O_2 .

For comparison reasons the spectrum acquired from an as-cleaned Si sample, which does not exhibit any oxide layer, is also shown in Fig. 4.2. The SiO_x layer thickness estimated from these XPS data was ~2 Å for the as-cleaned sample and ~8 Å for the heated and oxidized sample.

To check the uniformity and continuity of the grown Y_2O_3 thin film, the logarithm of the intensity of the underlying Si 2p peak corresponding to Si-Si bonds (the substrate)

versus $1/\sin\theta$, where θ is the take off angle, is plotted in figure 4.4 . As one can see, the acquired Si intensity shows a very good exponential attenuation with the take-off angle, indicative of the presence of a uniform and continuous film deposited on Si, even for such a small thickness.

From these XPS investigations, it appears that the most of the interfacial SiO_x layer forms during the ablation growth process, since the area corresponding to Si-O bonds is much larger in the sample with the Y_2O_3 layer, even when the substrate temperature was as low as 275 °C. Responsibility for this growth could be attributed to either the high energy oxygen atoms and ions from the laser plume, which can easily reach several tens of eV, or the presence of metallic Y atoms, which enhances silicon oxidation.

To study the influence of the oxygen pressure used during the PLD upon the thickness of the interfacial layer a set of four samples were grown. The deposition conditions and the thickness of the interfacial layer are shown in Table 4.1. Samples 3 and 4 were deposited with a hydrogen pretreatment and will be discussed later in this chapter.

Table 4.1 Processing conditions and characteristics of the interfacial layer of a series of Y_2O_3 films.

Sample No.	p(O ₂) mTorr	H ₂ clean	SiO _x thickness (Å)			Oxygen content (%)	
			VASE	XPS	HR-TEM	OII	OI
1	10	-	37	30	31	22.6	60
2	0.01	-	5	19	13	11.4	62
3	0.01	+	3	14	25	10.9	62
4	10	+	39	38	31	18.7	65

The SiO_x thickness values displayed in Table 4.1 were measured by VASE, estimated from HR-XTEM micrographs similar to those shown in figures 4.5 and 4.6 and calculated from XPS data [Mit94]. One can note that the agreement between these values is not very good. There are several explanations for this. Concerning VASE, one should keep in mind that the bulk optical constants used to fit the acquired optical data are certainly different from those of the thin films formed here [Her98]. Moreover, the Y_2O_3 films grown under low oxygen pressure exhibited rather poor optical data and the fit of ellipsometry data to known standards was more difficult and prone to errors. According to XPS data, the difference between the Si 2p peaks corresponding to Si-Si bonds and Si-O bonds was only ~1.8 eV. This indicates that the oxide layer is not stoichiometric SiO₂ [Her98], but a suboxide (this accounts for SiO_x notation used throughout this investigation). Secondly, some of the silicon oxide might be mixed with the deposited oxide. This could explain why the HR-XTEM micrographs exhibited sometimes a two-layer interfacial structure as shown in figure 4.5. However, XPS depth profiling investigations did not find any measurable sub-structure in the Y 3d peaks (located at

156.1 eV and 158.2 for all samples) which could indicate the formation of a suboxide or yttrium silicate layer [Kan99].

Detailed XPS scans of the O 1s region acquired from these 4 samples after their surface was sputtered-clean with 4 keV Ar ions for 2 min. are displayed in figures 4.7 and 4.8. The fitting of the acquired spectra required the use of two peaks, indicating the presence of two types of oxygen species in these films: one located at ~529.0 eV corresponding to the usual Y-O binding energy [Ing96, Dur90], denoted OI, and one located at ~531.3 eV, denoted OII in Table 4.1, which could be related to an oxyhydride phase or physisorbed oxygen. When using only the oxygen atoms corresponding to Y-O bonds to calculate the films stoichiometry one obtains a chemical composition that is 40-41% Y and 60-59% O, i.e. stoichiometric yttria. This fact suggests that the oxygen located at 531.3 eV is physisorbed. It is interesting to note that the thickness of the interfacial oxide layer correlates very well with the amount of this second peak. The higher the oxygen pressure used during the deposition, the higher the fraction of this peak and thickness of the interfacial layer (see Table 4.1).

Thin ZrO_2 films showed similar, loosely-bonded oxygen in the XPS spectra. This loosely bonded oxygen has been shown to contribute to the additional growth of the layer since ZrO_2 interfacial layers grew when annealed under high vacuum conditions (5×10^{-10} Torr) [How02] and this oxygen peak was reduced post-annealing.

From data shown in Table 4.1 one can see that the oxide thickness is larger for samples grown under higher oxygen pressures. This indicates that the interfacial layer forms because of a catalytic oxidation of Si induced by the presence of metal atoms and not because of the high energy oxygen ions or atoms from the laser plume (they are more

energetic for 10^{-5} Torr than for 10^{-2} Torr, where the mean free path is ~ 5 m versus ~ 0.5 cm).

To study the formation of the interfacial layer at the onset of deposition, a series of samples of differing thickness were grown from ultrathin samples to samples on the order of 10s of angstroms. As the deposition begins, a thin interfacial layer, of around 10 Å immediately forms. Figure 4.9 shows the plot of the logarithm of the intensities of the Si 2p peaks corresponding to Si atoms located within the substrate, Si^0 , and within the oxide interfacial layer, Si^{x+} , versus the reciprocal of the sine of the take-off angle from a sample that had a very thin (~ 9 Å) Y_2O_3 film deposited. The Si^0 peak intensities approximately show the expected logarithmic attenuation of a buried layer. The Si^{x+} peak intensities, on the other hand, are almost constant. This implies that the Si atoms bonded to oxygen are actually not entirely located at the Si/SiO_x interface but present within the surface region of the film. This result is indicative of some silicon diffusion during the early stages of growth.

Figures 4.10a and 4.10b show XRR spectra of Y_2O_3 films that are 50 Å and 80 Å thick, respectively. These samples were deposited to observe the growth of the interfacial layer as the film grows. The models that describe these layers and generated the overlapped fit curve for reflectivity are shown as insets in the top right corner of the figures. One can observe that the density of the interfacial layer has increased with the increased film thickness. This gives a good indication that there is a changing interfacial composition with deposition time, which implies that there is a complex diffusion process in which the silicon, oxygen and metal do not only meet at the interface between the Si and the interfacial layer but also throughout the thickness of the interfacial layer. XPS of

this data that was shown in figure 4.9 confirms that this is occurring from the onset of film deposition. Niu02 et al. found similar silicon diffusion into the upper interface of Y_2O_3 films using electron energy loss spectroscopy [Niu02] across the interfacial layer.

Typically, in the thermal oxidation of silicon, the Si/SiO₂ interface grows into the silicon, with the growth of the film governed by the transport of oxygen to the interface. If this were the case, and oxidation would be simply due to oxygen diffusion through the growing film to the interface, then the density and upper roughness of the interfacial layer would not change. Rather, we propose a more complex mechanism, in which the presence of the metal ions (Zr or Y) facilitates the rapid oxidation of silicon and increases the diffusion of silicon and oxygen to the upper interface. This would explain the growth and density change in the interfacial layer and the increased upper interfacial roughness that was observed in XRR and HR-XTEM. It has been observed that metallic atoms may enhance the oxidation rate of silicon [Kim97].

XPS data also shows that there are considerable changes in the stoichiometry of the interfacial layer with increased deposition time. Figures 4.11a and 4.11b are multiplex scans of the Si 2p region taken from the same samples as those shown in figure 4.10. By inspecting the relative ratios of the Si⁰ to Si⁺⁺, between the 50 Å and 80 Å films, one may see that the ratio of Si-O to Si areas has increased with layer thickness. Coupled with the previous XRR data, one can infer that there is oxidation as the film grows. Through XPS analysis, the amount of oxidized silicon present in these samples and the amount of oxidized silicon present in a silicon sample (figure 4.2b) that underwent the same thermal conditions without having a film deposited was compared. It was found that the interfacial layer present in between the film and substrate had a much greater thickness

than that of the oxidized silicon formed on the Si wafer. This implies that the interfacial oxide formed during deposition is of poorer quality than a thermally grown one and allows diffusion of silicon towards the top of the interfacial layer.

Low Temperature UV Ammonia pretreatment of Silicon

To prevent or at least retard Si atom migration to the film/interfacial layer upper interface during thin film growth, the substrate was exposed to NH_3 for several minutes to form a silicon nitride or oxynitride barrier layer. Since the thermal nitridation of Si proceeds very slowly at 600°C , the substrate was irradiated with a Hg lamp that emits 184.9 and 253.7 nm radiation to enhance the chemical reactions occurring at the surface. Figure 4.12 shows an XPS survey scan of the photoelectron spectrum from a sample that was irradiated with 2 Hg lamps at 100 Torr for 60 minutes. It shows the presence of nitrogen on the surface of the sample but also a strong presence of oxygen on the sample as well. As was noted in the literature survey, the presence of oxygen is almost always present during direct nitridation processes of silicon because any residual oxygen will be present in the film unless the oxygen composition in the deposition chamber is extremely low (>50 PPM).

The effect of an oxynitride surface layer on the density of the layer can be seen in figure 4.13, which shows that a nitrided film surface (from a sample measured to be ~ 10 Å) can demonstrate a change in the critical angle to that of a higher density layer. This shift in critical angle serves as evidence of a nitrided layer and one that is denser than silicon.

To estimate the amount of nitrogen that was present in the samples, a series of multiplex scans were taken for each of the elements examined in the film. The carbon on the films was assumed to be adventitious and was not included in a calculation of the

composition of the films. Each multiplex scan was fitted using a series of Gaussian peaks and the integral of these peaks divided by a sensitivity factor for that element were used as measures of that composition of the film. Figure 4.14 shows the multiplex scan from the nitrogen within the surface of the sample. The peak value of 397.8 eV (corrected for carbon displacement) corresponds well to Si-N bonding that was noted in the previous chapter.

Figure 4.15 shows the multiplex peak for oxygen bonding in the oxynitride film. The peak is deconvoluted into two peaks. One, at lower binding energy of 530.5 eV, corresponds to bonding with silicon-oxygen bonding at the interface and displayed a 1:1 atomic concentration with Si^{1+} (see below). It will be labeled in subsequent analysis as O_x . The more intense peak corresponds to oxygen bonding with silicon through the bulk of the film and may also have a contribution from bonding with the adventitious carbon to its intensity. It is located at a value of 532.3 eV. It will be labeled in subsequent analysis as O.

Figure 4.16 shows the XPS multiplex peak for the silicon substrate. The analysis used divided the silicon substrate into 4 peaks, labeled A, B, C, and D. Peaks A and B are set constant and correspond to the substrate peak. In all analysis, peak B was set as having exactly half the intensity of peak A, which corresponds to the peak splitting of the 3/2 and 5/2 orbitals and would be apparent with a higher resolution scan. Peak C is fitted to the Si^{1+} peak that corresponds to interfacial SiO_x . Peak D is due to the shift in Si 2p binding energy corresponding to a silicon oxide or nitride layer. Attention was not focussed on deconvoluting this peak into nitride and oxide components.

Using the multiplex data for a variety of different deposition conditions which included changes in the deposition time, number of lamps used to irradiate the sample and the partial pressure of ammonia in the chamber, the relative atomic percents of silicon, oxygen and nitrogen in the oxynitride films were calculated following equation 3-6. This may be seen in Table 4.2. All samples were grown at a substrate temperature of 600 °C.

Table 4.2 Relative atomic concentrations of oxynitride thin films grown under different deposition conditions including time, ammonia partial pressure and lamp power.

Sample	Ammonia Pressure	Time	# lamps	Relative Concentration (at%)				
	(Torr)	(min)		Si ¹⁺	Si ⁴⁺	N	O	O _x
1	10	10	4	3.0	17.6	8.5	67.3	3.6
2	100	10	4	4.7	16.1	10.5	65.7	3.0
3	10	60	2	3.1	18.4	5.8	67.8	4.8
4	100	60	2	3.3	17.1	8.3	67.2	4.2
5	0.1	10	1	N/A	N/A	N/A	N/A	N/A
6	1	10	1	3.3	15.7	1.4	75.2	4.4
7	1	10	0	5.1	14.2	0.6	76.0	4.0
8	100	5	4	3.5	15.5	12.2	63.7	5.1
9	100	20	4	4.2	14.0	9.2	58.7	13.8

It may be noted that sample 5 which was grown at 0.1 Torr of ammonia, the nitrogen composition was almost zero, and no atomic percentages were calculated for this sample. Several trends in the amount nitrogen incorporation from this data can be seen relative to processing conditions. Firstly, samples that were deposited at high ammonia pressure tended to have the most nitrogen incorporation into the film. Secondly, the increase in lamp power (as a function of number of lamps) tended to increase the amount of nitrogen incorporated into the films. A sample that was annealed in ammonia (sample 7) with no UV irradiation had a negligible amount of nitrogen in the film. Samples that were

photodeposited for 60 min with 2 lamps had lower nitrogen compositions than 4 lamp samples deposited for 10 minutes.

Several further observations about these samples has to do with the oxygen content. Except for the anomalous sample 9, the O_x composition had nearly a 1:1 ratio to the Si^{1+} peak, which denotes some sort of interfacial bonding of silicon to oxygen. Secondly, the ratio of the concentration of the Si^{4+} to O in these peaks does not have a 2:1 ratio. Rather, there seems to be a large amount of extra oxygen that may be bonded to adventitious carbon.

The thickness of these ultrathin oxynitride samples were calculated using equations 3-4 and 3-5 for a 90° take-off angle. These results are displayed in Table 4.3.

Table 4.3 Thickness values as measured by XPS for a series of oxynitride thin films.

Sample	Ammonia Pressure	Time	# lamps	Thickness
	(torr)	(min)		(nm)
1	10	10	4	1.33
2	100	10	4	1.30
3	10	60	2	1.74
4	100	60	2	1.63
5	0.1	10	1	1.19
6	1	10	1	1.21
7	1	10	0	0.97
8	100	5	4	1.17
9	100	20	4	1.22

Table 4.3 shows that the growth rate of these films is very resistant to lamp power, partial pressure of ammonia in the film and time. The thickness of the 60 minute long films were slightly larger than the ten minute exposed films, but the changes in the thickness values are negligible. This may be due a low general oxidation rate that occurs

600 °C. However, Boyd et al. observed a oxidation rate for low-pressure UV lamps under an atmosphere of oxygen at 550 °C to be near 50 times the dry thermal oxidation at a temperature of 900 °C [Boy93]. Thus, considering that there is oxygen contamination within the chamber, there is the possibility at least that some UV-induced oxidation would take place in these samples. Nevertheless, the presence of nitrogen within these films limits the growth of the films to under 2 nm despite 1 hour of exposure to UV irradiation. This may be considered some evidence the silicon diffusion from the substrate and oxygen diffusion from the ambient is limited when an oxynitride containing as low as 10 at% N is deposited on the film.

The development of a suitable, ultrathin, diffusion barrier to silicon oxidation would bode well for the prevention of interfacial reaction during the deposition of high-k dielectric layers. The thickness values from these layers are well suited to the deposition of a high-k layer on top of these oxynitrides. In addition, the deposition of nitrided UV layer at considerably lower processing temperatures is an advantage for device engineering.

Effect of Silicon Nitridation Pretreatment on Interfacial Layer Formation

In order to determine the effect of pretreating the silicon surface with ammonia in UV on interfacial layer formation, the oxynitride sample with the highest nitrogen content was selected. The optimum conditions for this pretreatment were: 20 minutes, 4 lamps, and 100 Torr ammonia. The rationale for this decision was that the amount of nitrogen in the sample corresponds to an increased stopping power for silicon and oxygen diffusion.

Figures 4.17a and 4.17b show the XRR spectra for ZrO_2 films grown at 600 °C with no nitridation and pre-nitridation treatments, with their accompanying fits and model parameters. According to the simulation of these spectra, the thickness of the interfacial

layer was significantly decreased from 18 Å to ~8 Å, while the density of the interfacial layer changed from 2.38 g/cm³, which is much closer to SiO_x stoichiometry, to 2.76 g/cm³. This is indicative of nitrogen incorporation into the interfacial layer chemistry since the density of Si₃N₄ is 3.17 g/cm³ while the density of amorphous SiO₂ is 2.2 g/cm³ [Crc97].

Figure 4.18 is an XPS scan from the Si 2p region of two Y₂O₃ samples that had identical deposition conditions showing the change in thickness and chemistry of the interfacial layer with the pre-nitridation treatment. The ratio of the relative heights of the Si^{x+} to the Si⁰ peak decreased for the surface treated sample, which indicates the presence of a thinner interfacial layer. In addition, there is a shift in the binding energy of the Si^{x+} peak, which is attributable to an increase in the number of Si-N bonds, also evidenced by the presence of a N1s peak in the XPS spectra.

Effect of Hydrogen Pretreatment of the Silicon Surface

A high temperature hydrogen treatment was performed in order to reduce the amount of initial oxidation that occurred while the sample was heated to temperature.

The C-V and I-V characteristics of the samples described in table 4.1 are displayed in figures 4.19 and 4.20. The highest dielectric constant, estimated from the value of the capacitance in the accumulation region of a thick layer, had a value of 14. This value is quite similar to that of bulk Y₂O₃. The use of much lower oxygen pressures than the optimum value of 10 mTorr resulted in a marked degradation of the electrical properties.

One can see from Table 4.1 that H₂ anneals had just a marginal influence upon the thickness of the interfacial layer. This is further proof that this layer was formed during deposition and not prior to it. However, the C-V and I-V characteristics of samples that received this H₂ clean were improved. Probably this treatment helped passivate the

monolayer coverage SiO_x already formed on the sample surface. Samples exhibiting thin SiO_x interfacial layers also exhibited large leakage currents. It appears that the columnar structure of the grown Y_2O_3 layers, identified from TEM studies, is responsible for the high values of the leakage current. It is further suggested that the once the interfacial layer was thicker than $20 \text{ \AA}$, a significant decrease of the leakage current was observed. Although its presence degrades the overall dielectric constant, it might be necessary to contribute to low leakage currents.

Low-Temperature Growth of Indium Tin Oxide

The deposition conditions employed for the ITO samples are shown in Table 4.4, which also includes whether or not the samples were irradiated by UV (+/-). In addition, the thickness (t_v) as measured by spectroscopic ellipsometry (VASE), the thickness (t_x) measured through x-ray reflectivity (XRR), roughness of the layers, i.e., the silicon/interfacial layer, interfacial/ITO layer and the surface roughness of the film as represented by σ , and the densities (ρ) of the interfacial and ITO layers are included. The ellipsometry model used was a simple ITO layer on top of a SiO_2 interfacial layer and acted as an important guide for the subsequent reflectivity analysis.

The thickness, roughness and densities of the films that were measured by x-ray reflectivity were simulated with the Philips WinGixa™ software. The values were iterated until a very good fit ($\chi^2 < 0.01$) was obtained. In order to do this, the presence of some interfacial reaction layer between the silicon and the ITO films had to be inserted as part of the simulation. While a density value for a layer under $20 \text{ \AA}$ may be problematic to measure, this layer density reflects the presence of a silicon-oxide-ITO interfacial reaction layer. An example of one of the XRR plots with a superimposed simulation that employs the values listed as the inset in figure 4.21 is shown below for sample ITO 7.

Table 4.4 Deposition conditions and thickness, roughness and density values estimated from spectroscopic ellipsometry (only for t) and x-ray reflectivity modeling.

Sample No.	Dep. Temp. (°C)	UV	t_v (Å) VASE	t_x (Å) XRR		σ (Å)			ρ (g/cm ³)	
				int	ITO	Si	int	ITO	int	ITO
ITO 1	50	+	259	9	229	2	3	7	3.77	6.80
ITO 2	100	+	248	12	232	5	10	3	4.58	7.00
ITO 3	150	+	250	12	221	7	5	4	2.15	7.00
ITO 4	150	-	252	7	225	4	7	4	2.23	6.94
ITO 5	100	-	247	10	214	7	8	2	4.27	6.98
ITO 6	50	-	247	7	218	7	10	3	4.40	7.00
ITO 7	220	+	--	5	437	5	15	3	3.42	7.02
ITO 8	220	-	--	5	440	7	13	3	3.51	7.18
ITO 9	220	+	--	--	--	--	--	--	--	--
ITO 10	220	-	--	--	--	--	--	--	--	--

One can see that the thickness values obtained from XRR simulation closely match those obtained from VASE. The surface roughness values obtained showed that the films were very smooth, regardless of the deposition temperature.

Figure 4.22 shows the optical transmittance for ITO 10. As can be seen here, the optical transmittance approaches 90% for this sample. Resistivity values for this sample were calculated based on the growth rate of the samples (not measurable by our techniques for samples 9 and 10) and the V/I results obtained by a four point probe to be about $3.4 \times 10^{-4} \Omega \text{ cm}$.

The structure of the samples that were deposited at 50 °C and 100 °C were found to be amorphous by both GIXD and TEM imaging and diffraction, regardless of the UV conditions. Figure 4.23 is a bright-field (BF) image of sample ITO 1 with accompanying selected area diffraction pattern (SADP). The image shows no diffraction contrast and an amorphous ring is clearly visible. The crystalline dots in the background originate from the silicon substrate.

It may be noted that the UV irradiation had a profound effect on the structure of the samples that were deposited at or above 150 °C. In a comparison between samples ITO 3 and 4, GIXD revealed the presence of a rather wide peak at a 2 theta value of 31°, which corresponds to near the (222) reflection in a fully crystallized ITO film. There was some hint of a crystalline peak in the UV sample but it was difficult to be completely certain of the presence of crystallites in the UV samples. They were examined and confirmed by plan-view TEM. Figure 4.24 is a bright field image from ITO 3 showing the presence of crystallites of the size of approximately 10-20 nm with a polycrystalline SADP while figure 4.25 is a BF image of sample ITO 4 with inset amorphous ring pattern. Clearly, the effect of UV is significant for this deposition temperature as the non-thermal energy source has induced crystallization within the sample.

For the higher deposition temperature samples, ITO 7 and ITO 8, the effect of UV irradiation is also quite pronounced. Grazing incidence XRD taken from sample 7 and 8 showed that there is both strong texture emerging in the UV-radiated sample, with a (222) peak showing a much higher value relative to the other peaks, as compared with the non-UV sample. In addition, as can be seen from figure 4.26, there is a decrease in the FWHM of the (222) peak that clearly shows enhanced crystallinity in the UV sample. TEM analysis of these samples is shown in figure 4.27 and figure 4.28 for samples ITO 7 and ITO 8 respectively. It can be clearly seen that the presence of the UV effect during the deposition encourages the growth of the ITO grains. It may be postulated that the UV may have an even more pronounced effect as the deposition temperature shifts higher. This result and those on optical and electrical properties must be studied in greater detail in order to explain the effects of UV-irradiation during deposition of ITO.

Samples ITO 9 and ITO 10 also showed the effects of UV irradiation, in that the FWHM of the (222) peak was significantly decreased with UV irradiation. It is interesting to note that the peak position shifts in the opposite direction as that samples that are deposited on the silicon substrates. This peak shift may deal with the thermal mismatch of the ITO with the relative substrates, or may have to do with changes in oxygenation within the samples. This is another possibly fruitful area to explore the effects of UV irradiation. The effect of UV irradiation could be due to a twofold process. Firstly, the presence of a non-thermal energy source to increase the mobility of the surface atoms during the deposition could lower the activation energy required for crystallization and growth of the ITO films. In addition, the presence of ozone and atomic oxygen from the UV-induced reaction could change the oxygen composition of the film. This difference may affect the final microstructure that was observed.

In order to confirm the effects of laser irradiation on the structure of the UV irradiated and the nonirradiated portions of the ITO films above the crystallization temperature, a set of films were deposited at substrate temperatures of 180 °C and 220 °C on silicon and coming glass substrates. To show the pronounced effect of UV on the microstructure at temperatures close to the crystallization point. Figure 4.29 shows a plan view TEM image comparing the ITO films deposited at 180 °C. It can be seen by comparing the two samples that the grain size at this temperature did indeed increase, confirming the previous results. In this case, the median grain diameter increased about twofold, from an average grain diameter of 200 nm to 400 nm. The microstructure appeared to be a single phase microstructure and figure 4.30 shows a $B=\langle 111 \rangle$ diffraction pattern that corresponds to In_2O_3 .

In order to confirm whether the UV illumination affects the nucleation properties of the films or the grain growth of the film. The film that was deposited at 180 °C was annealed at 180 °C for 20 minutes under UV-illuminated conditions at 10 mTorr O₂. The microstructures of the films were compared. Figure 4.31 shows that annealed sample versus the as-deposited sample. It can be seen here that there is no considerable change in grain size of the films after a UV anneal. Thus, the effect of photonic excitation may be considered to be a function of nucleation density. The energetic oxygen and increase in adatom surface migration causes a decrease in nucleation density and the atoms have a more difficult time attaching to stable clusters that become nuclei.

For samples that were deposited at a higher temperature, the microstructure is not so easy to interpret. Figure 4.32 shows the microstructure of the ITO films when they are deposited at 220 °C. It can be seen that there is a slight increase in grain size, but the effect is not as dramatic as with the previous samples deposited at 180 °C. Also, the microstructure deposited at 180 °C had a coarser structure than the microstructure deposited at 220 °C in general. The 220 °C non-UV had the appearance of a dendritic phase, with some of grains elongated. The microstructure appeared similar to the microstructure that appeared in the Naka et al. paper of an 200 °C air-annealed microstructure containing a complex mixture of SnO (described by the authors as having a crystallographic shear structure) and In₂O₃ [Nak00].

Figure 4.33 is a graph that shows the resistivity as a function of temperature. It can be seen here that the samples deposited using UV-irradiation had a significantly lower resistivity value than those deposited without using UV irradiation. This could be due to the grain size effect. It is also worth noting that the complex, multiphase, higher

temperature microstructure had a higher resistivity than the lower temperature. This effect may be due to the overall presence of a finer phase that nucleated within the film and may also be due to incomplete chemical bonding of oxygen in the samples.

Figure 4.34 is a plot of the optical transmittance for all four samples. It can be seen that the 220 °C non UV (the highest resistivity film) had the poorest transmittance, which corresponds to the resistivity measurements that coincide with a more metallic nature. It can be seen that UV irradiation restored the transmittance profile to one that is similar to the other films that were processed with high transmission in the visible region. It appears that the samples with the least number of grain boundaries had the best transmittance and electrical values.

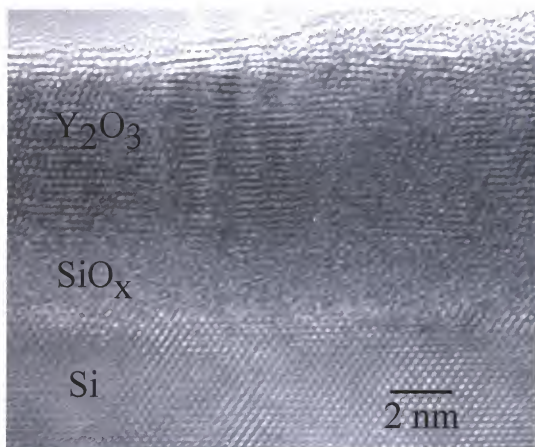


Figure 4.1 High-resolution cross-section TEM image from a laser ablated Y_2O_3 film showing the presence of an SiO_x interfacial layer with a rough interface.

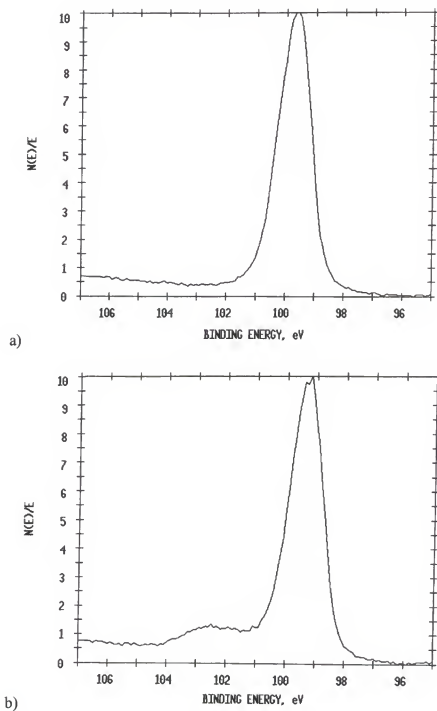


Figure 4.2 XPS high resolution scans of the Si 2p region acquired from (a) an as-cleaned sample and (b) a Si sample heated at 550 °C for 30 min under a 10 mTorr oxygen partial pressure.

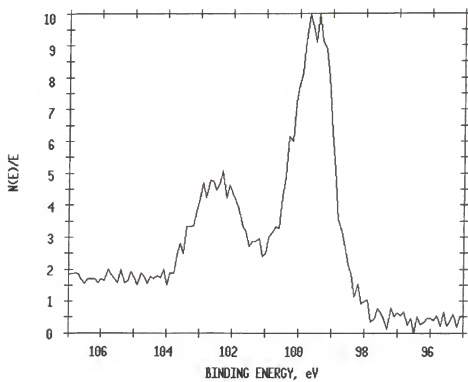


Figure 4.3 XPS high-resolution scan of the Si 2p region acquired from a Si sample with a ~ 40 Å Y_2O_3 layer grown at 275 °C.

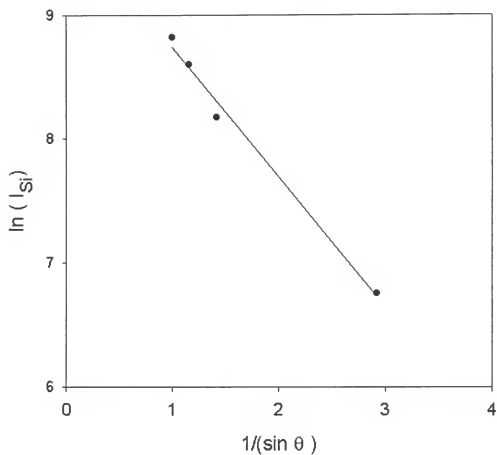


Figure 4.4 Plot of the logarithm of the underlying Si peak intensity versus take-off angle of the sample covered by a ~ 40 Å thick Y_2O_3 film.

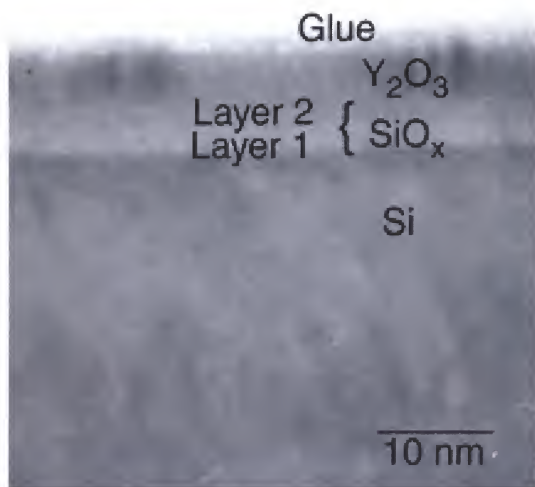


Figure 4.5 HR-TEM micrograph of Y₂O₃ taken from a B=[011] zone axis in the silicon with a double layer interfacial oxide for sample 1

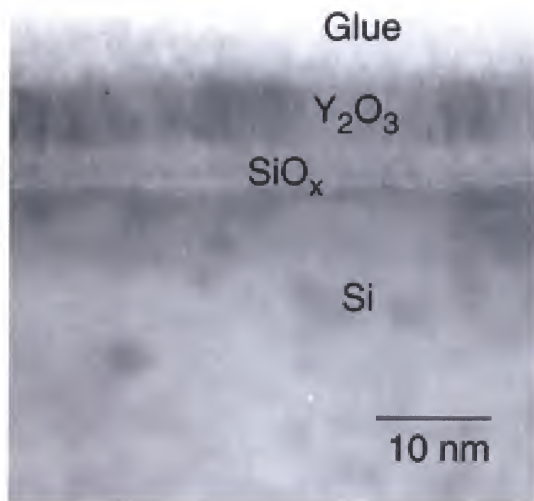
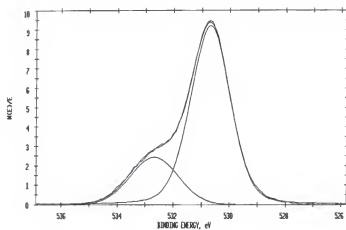
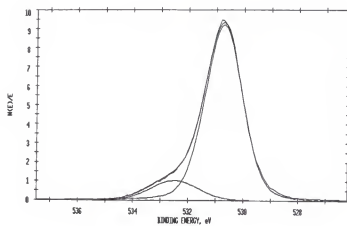


Figure 4.6 HR-TEM micrographs of Y_2O_3 taken from a $B=[011]$ zone axis in the silicon with a single layer of SiO_x for sample 4.

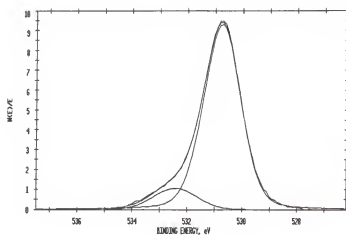


a)

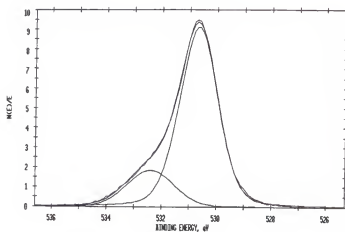


b)

Figure 4.7 XPS high resolution scans of O 1s region acquired from the samples shown in Table 4.1 for a) sample 1 and b) sample 2.



a)



b)

Figure 4.8 XPS high resolution scans of O 1s region acquired from the samples shown in Table 4.1 for a) sample 3 and b) sample 4.

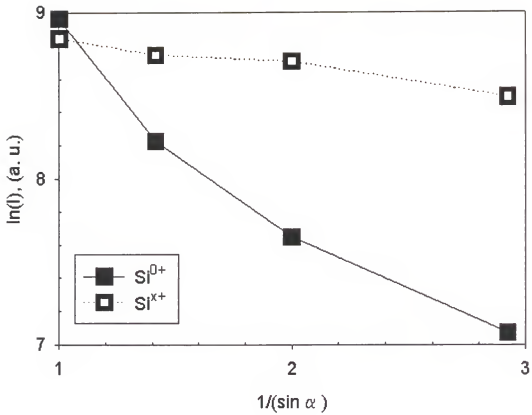
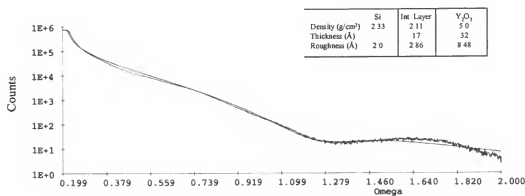
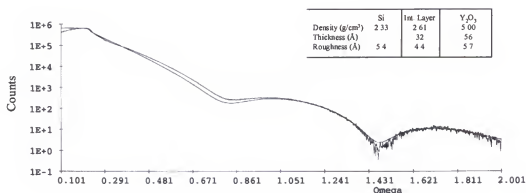


Figure 4.9 Plot of the logarithm of the Si 2p peak intensities versus $1/\sin\theta$ (θ is the take off angle) of a sample covered by a $\sim 9 \text{ \AA}$ thick Y_2O_3 layer.



a)



b)

Figure 4.10 X-ray reflectivity curves and modeling fits the growth of the interfacial layer and density change for a) 50 Å and b) 80 Å Y₂O₃ films. The models indicate an increased density, interfacial layer thickness and upper interfacial layer roughness, which are signs of the silicon diffusion.

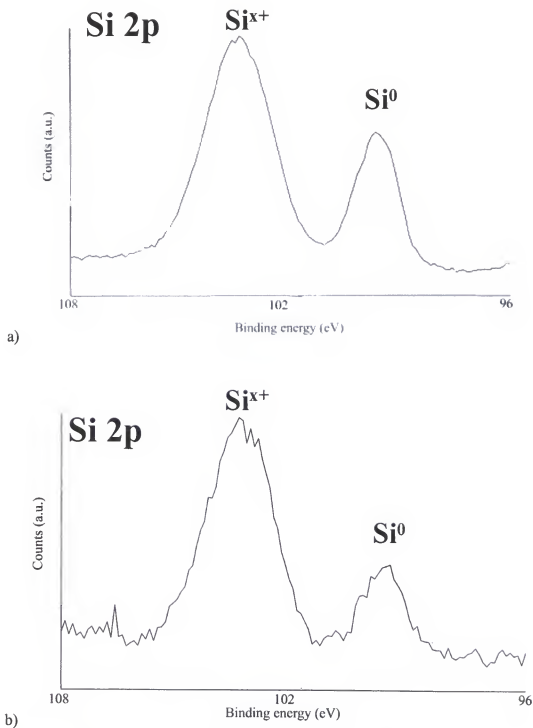


Figure 4.11 XPS spectra of the Si 2p region showing the Si^0 to Si^{x+} ratio for a 50 Å Y_2O_3 films and b) an 80 Å film.

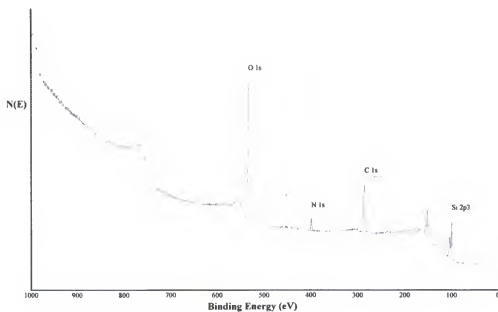


Figure 4.12 XPS survey scan of an ultrathin silicon sample nitrided in the presence of ammonia at 100 Torr using 2 Hg lamps for 60 minutes. The presence of the nitrogen oxygen and oxidized silicon and the silicon substrate may be seen from the spectrum.

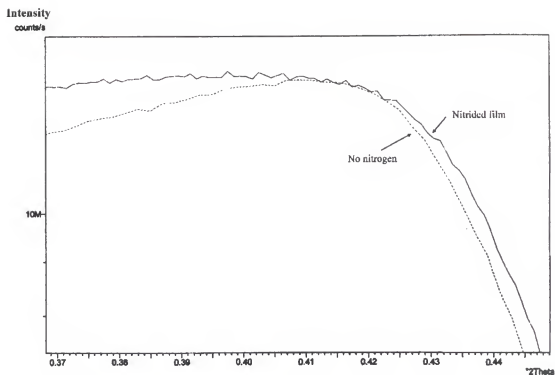


Figure 4.13 XRR spectrum zoom of the critical angle region showing the increase in critical angle and thus density of the film as a result of direct silicon nitridation.

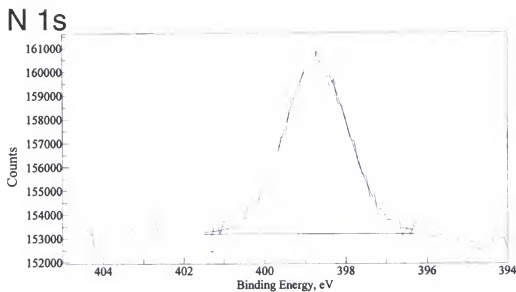


Figure 4.14 Multiplex scan from the N 1s region of an oxynitride film grown under nitridation conditions of ammonia at 100 Torr with 2 Hg lamps for 60 minutes. Count integrals from fits for these peak values were used to estimate the concentration of nitrogen species in the oxynitride films.

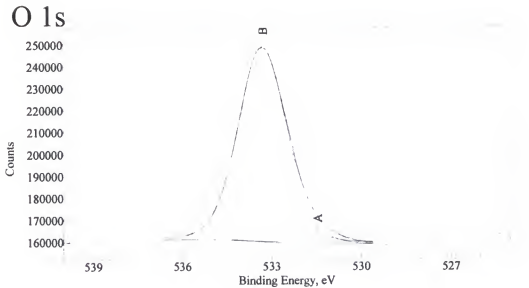


Figure 4.15 XPS multiplex scan from the O 1s peak showing the deconvolution of the peaks into the different chemical bonding states for silicon oxynitride. Peak A corresponds to interfacial bonding with silicon Si^{1+} and peak B corresponds to oxygen bonding to Si^{4+} in the oxynitride film and any C-O bonding on the surface of the film.

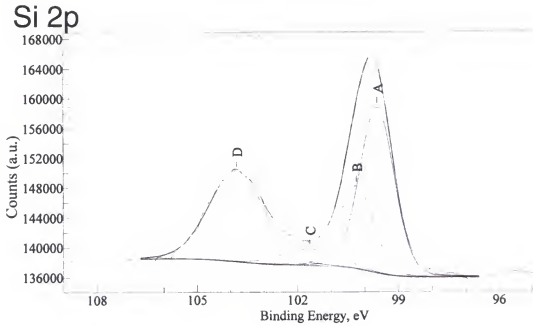
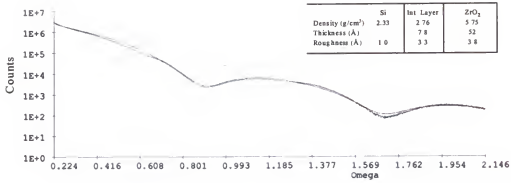
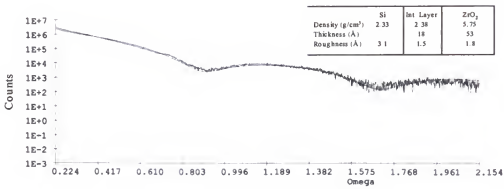


Figure 4.16 XPS multiplex scan from the Si 2p energy region showing the deconvolution of the peaks into the different chemical bonding states for silicon oxynitride. Peaks A and B correspond to the Si 2p $3/2$ and $5/2$ orbitals. Peak C corresponds to interfacial bonding of silicon and peak D corresponds to Silicon 4^+ bonding to oxygen and nitrogen. Integrated intensities of these peaks were used to measure film composition and thickness.



a)



b)

Figure 4.17 XRR curves of a ZrO₂ films a) deposited on pre-nitrided Si surface and b) on a bare Si substrate.

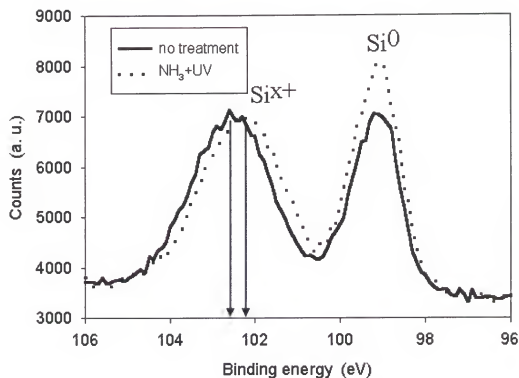


Figure 4.18 XPS spectra showing both a chemical shift and a change in relative heights of the Si peaks after Si nitridation before deposition of a ZrO₂ film.

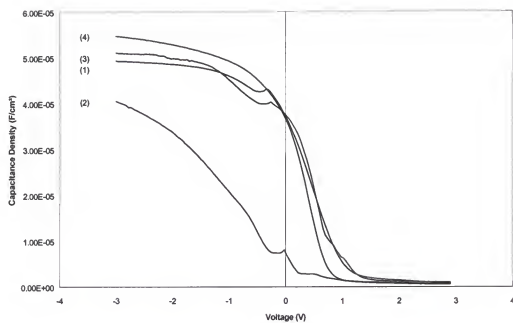


Figure 4.19 C-V Electrical characteristics of the four samples

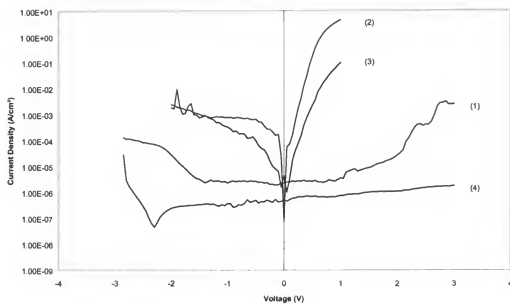


Figure 4.20 I-V Electrical characteristics of the four samples

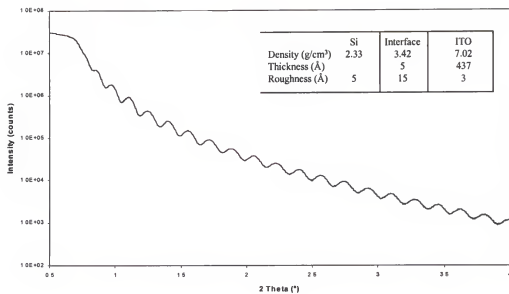


Figure 4.21 X-ray reflectivity graph from ITO 7 sample with inset film structural model.

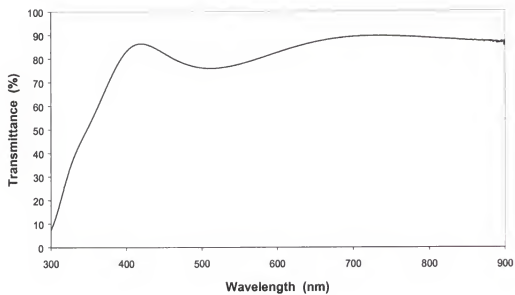


Figure 4.22 Optical transmittance of sample ITO 10.

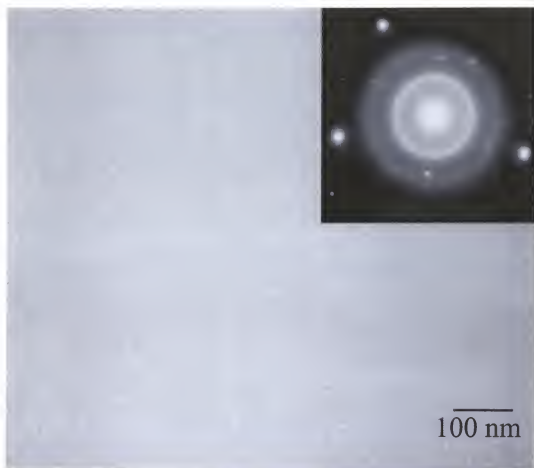


Figure 4.23 Amorphous ITO 1 film with inset diffraction pattern. Spots in the SADP come from silicon substrate.

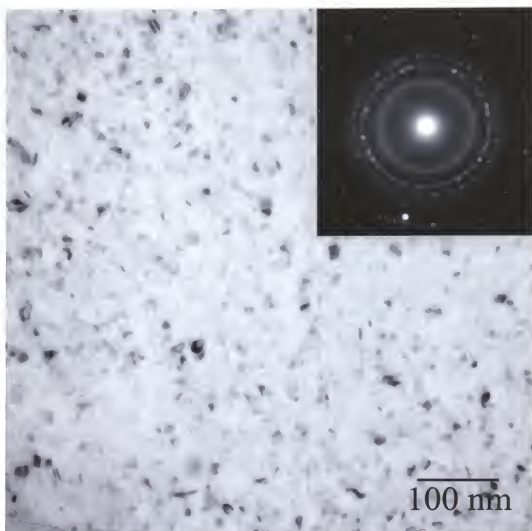


Figure 4.24 Bright field TEM with inset diffraction patterns from crystallized ITO 3

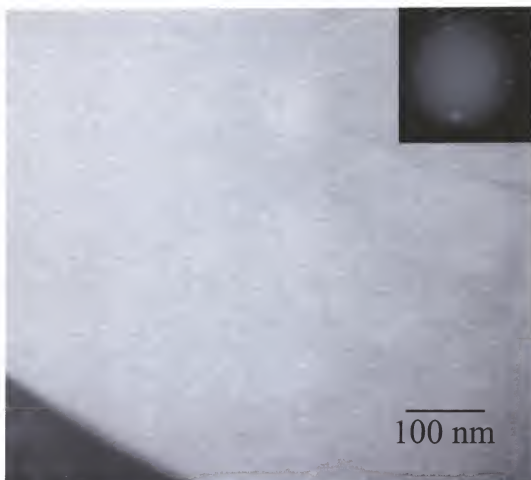


Figure 4.25 Bright field TEM with inset diffraction patterns of amorphous ITO 4.

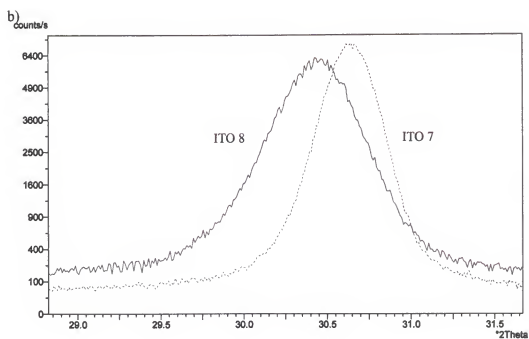


Figure 4.26 Comparison of the (222) diffraction peak as measured by GIXD of ITO 7 (UV) vs. ITO 8 (non-UV) showing an increased crystallinity in the UV sample.

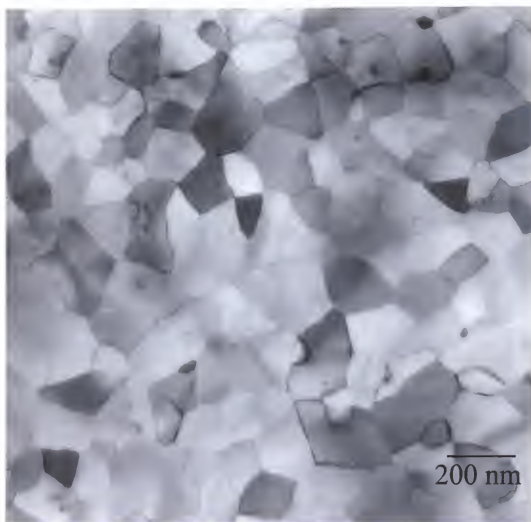


Figure 4.27 Bright-field TEM image from ITO 9 (UV)

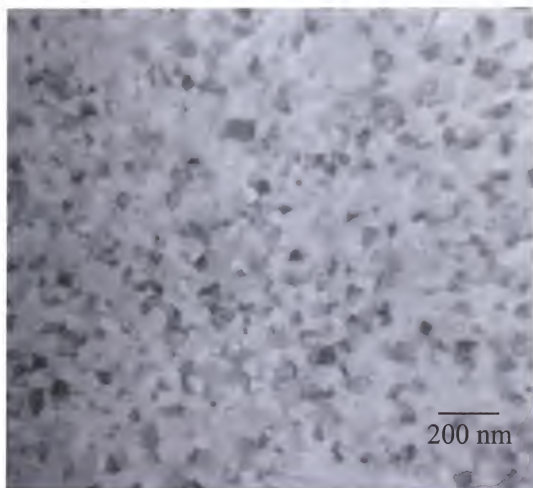


Figure 4.28 Bright-field TEM image from ITO 10 (non-UV)



Figure 4.29 BF TEM images showing increased crystallinity between a) a non-UV deposited sample and b) a UV-deposited sample at 180 °C.

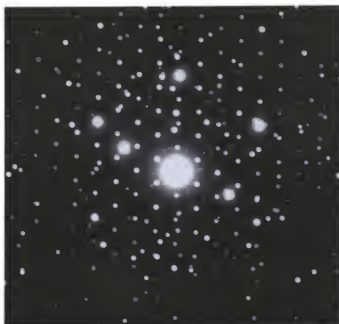


Figure 4.30 Selected area diffraction pattern from 180C with a $B=\langle 111 \rangle$ orientation corresponding to In_2O_3 from an isolated grain.

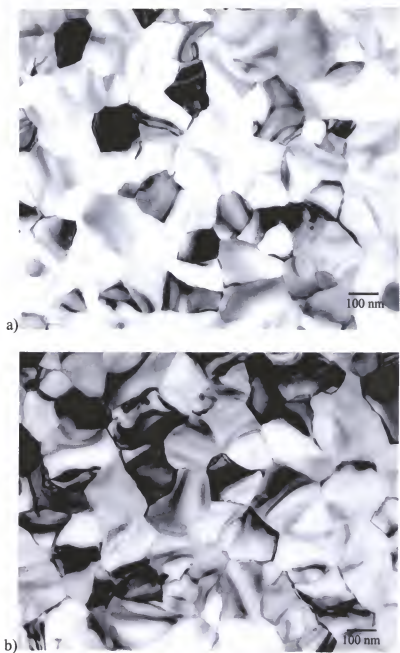


Figure 4.31 Comparison between a) as-deposited microstructure and b) UV-annealed microstructure for 180 °C. There is no appreciable difference in grain size.

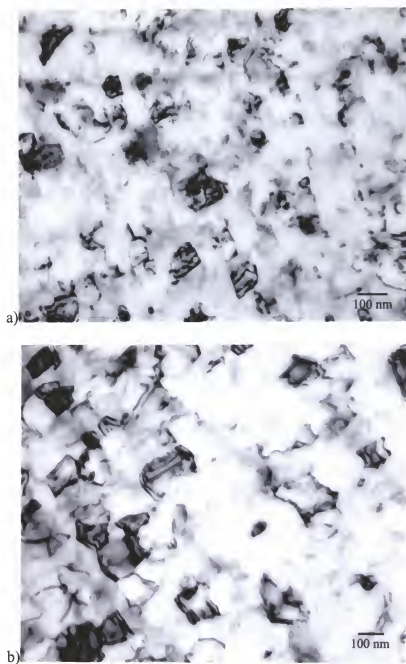


Figure 4.32 BF TEM images showing increased crystallinity between a) a non-UV deposited sample and b) a UV-deposited sample at 220 °C. The grain structure is more complex although UV tended to have a larger grain size.

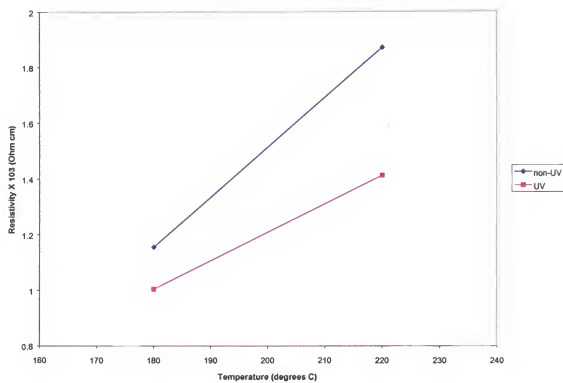


Figure 4.33 ITO film Resistivity as a function of temperature for the UV and non-UV cases.

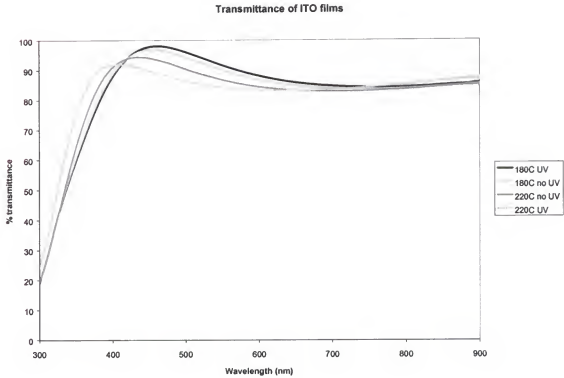


Figure 4.34 Optical transmittance values for UV vs. non-Uv at 180C and 220C. The higher the number of grain boundaries, the worse the transmission.

CHAPTER 5 CONCLUSIONS

High K dielectric thin films were pulse laser deposited on silicon and the interfacial layer between the film and substrate was characterized as to the extent of its nucleation and growth relative to temperature and oxygen partial pressure. X-ray reflectivity and x-ray photoelectron spectroscopy were used to show that there was excess physisorbed oxygen within the film, which may be located within the film in the lattice or within the grain boundaries of the film.

The interfacial layer grows with increasing film thickness. At the onset of deposition, silicon bonded to oxygen does an attenuated signal beneath the growing film, which means silicon is intermixing in the growing layer as soon as deposition begins. The amount of oxidized silicon is far greater in the interfacial layer than in a sample that underwent the same thermal and ambient conditions without having a film deposited upon it. It appears that metal atoms and silicon diffuse to the upper interface of the interfacial layer and react there.

Silicon oxynitride films were deposited at 600 °C using various processing parameters such as lamp power, ammonia partial pressure and deposition time. Oxygen was present in all of the films deposited. It was found that the layers underwent self-limiting growth. However, nitrogen content within the films increased with increasing lamp power and increasing ammonia pressure.

Silicon nitride pre-treatments before film deposition had the dual decreasing the thickness of the interfacial layer and increasing the density of the interfacial layer

towards that of silicon nitride. In addition to this, the oxynitride film acts as a diffusion barrier to the movement of silicon, metal and oxygen in the growing film.

Samples that were processed with a high-temperature hydrogen anneal displayed a very thin interfacial layer and had the effect of passivating the film from poor deposition thermal oxide formation. This allowed an increase in capacitance of the film relative to films that had no hydrogen pretreatment.

Indium tin oxide films were processed using mercury-lamp assisted pulsed laser deposition. It was found that the use of UV lowered the deposition temperature, increased the crystallinity of the film. It was found that UV has the advantage of increasing nucleation density during film formation. High quality films were deposited at a low temperature that had refractive indexes, extinction coefficients, and resistivities that were comparable to some of the best values produced in the literature at higher temperatures.

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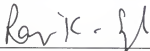
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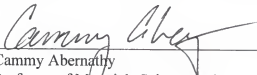
Nabil Bassim is engaged to be married in early 2003 to his loving fiancée, Carol. His interests include politics, sports, music and cinema.

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